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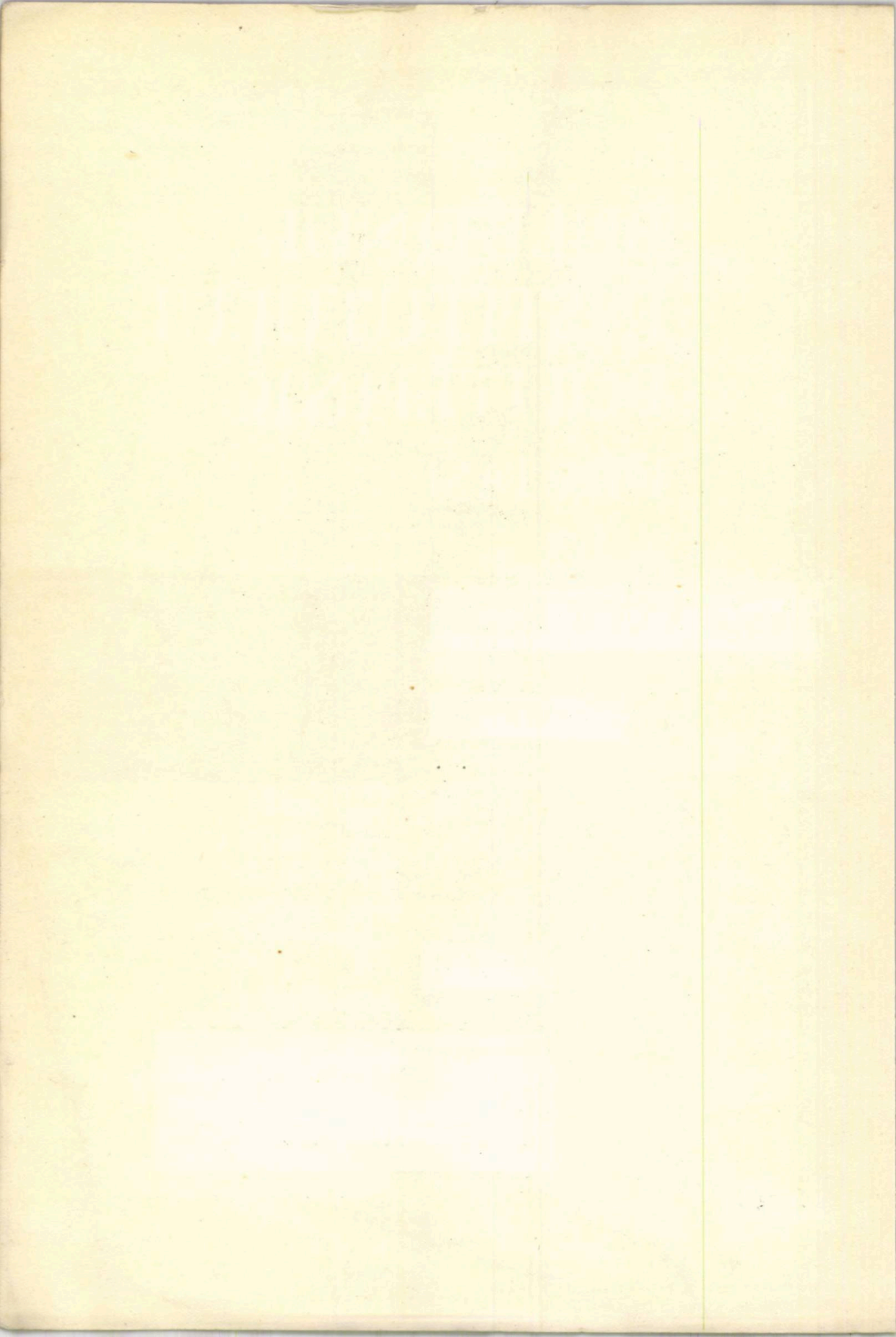
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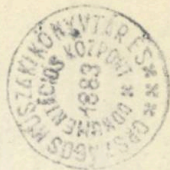
Fasc, 1—2

Secția II

CHIMIE
ȘI
INGINERIE CHIMICĂ

1981





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Secția II

**CHIMIE
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INGINERIE CHIMICĂ**

1981

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Tom XXVII (XXXI), fasc. 1-2

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COMBINAISONS COMPLEXES DU TI(III) AVEC DES LIGANDS DU TYPE DES HETEROCYCLES ORGANIQUES

II. SPECTRES D'ABSORPTION DANS L'ULTRA-VIOLET ET VISIBLE

PAR

I. BERDAN et N. CALU

1. Partie théorique

Dans un travail antérieur ont été présentés les résultats expérimentaux concernant la synthèse et quelques propriétés d'une nouvelle série de combinaisons complexes du TI(III) avec les ligands du type des hétérocycles organiques contenant l'atome d'azote donneur [1]. En poursuivant cette étude, dans ce qui suit sont exposés les résultats acquis concernant l'interprétation des spectres électroniques d'absorption de la série ci-dessous des combinaisons complexes synthétisées, ayant les formules générales: $TIX_3 \cdot 2ABT$, $TIX_3 \cdot 2BT$, $TIX_3 \cdot 2QUIN$, $TIX_3 \cdot 2PIC$, $TIX_3 \cdot 3NIC$, $TIX_3 \cdot 3INIC$ et $TIX_3 \cdot ADIP$, où $X = Cl, Br, I$, $ABT = 2$ -aminobenzthiazol, $BT =$ benzthiazol, $QUIN =$ quinoxaline, $PIC =$ l'acide picolinique, $NIC =$ l'acide nicotinique, $INIC =$ l'acide isonicotinique et $ADIP = 2,2'$ -azodipyridyle.

Si pour les espèces complexes de type $[TIX_n]^{+3-n}$, où $X = Cl, Br, I$, les spectres électroniques sont interprétés comme étant générés par des transitions halogènes $(\pi) \rightarrow$ métal (a_{1g}) [2]...[4], dans le cas des complexes du TI(III) avec les ligands organiques contenant l'atome d'azote donneur il faut prendre en considération la contribution d'autres types de transitions telles comme celles qui sont dûes au transfert de charge intermoléculaire ligand $\rightarrow TIX_3$. Les dernières transitions peuvent être édifiantes pour la détermination de la nature des espèces complexes formées dans les systèmes de réaction pris en considération. Par exemple, dans les systèmes de réaction du TI(III) avec des ligands organiques de type $R-NH_2$, on a mis en évidence la formation, en solution aqueuse, de quelques „complexes moléculaires“, de rapport molaire réduit, 1:1 [5]...[7]. Ceux-ci présentent dans le spectre visible des bandes à transfert de charge caractéristiques qui expliquent le transfert de charge intermoléculaire ligand $\rightarrow$ TI(III), le premier partenaire à rôle de base Lewis et le deuxième, un acide Lewis. Par conséquent l'interprétation des spectres électroniques des complexes synthétisés fournissent des informations utiles concernant le mode de coordination des ligands et la structure des espèces complexes formées.

2. Partie expérimentale

Les spectres électroniques des complexes du Tl(III) ont été obtenus à l'aide d'un spectrophotomètre de type Specord UV-VIS à l'enregistrement automatique. Une partie des déterminations spectrales dans le domaine visible ont été effectuées avec un appareil de type Specol. L'étalonnage des appareils a été réalisé à l'aide des solutions standard telles comme $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ et K_2CrO_4 .

Les complexes thalliques ont été purifiés par des recristallisations fractionnées. Les déterminations ont été effectuées sur des solutions, en utilisant des solvants adéquats, à la température ordinaire. La concentration des solutions analysées a varié entre $5 \cdot 10^{-2}$ M et $5 \cdot 10^{-5}$ M. L'épaisseur de la cuve utilisée, 1 cm.

3. Résultats et discussions

L'étude des spectres électroniques est basé sur l'analyse des modifications qui se produisent dans la position et l'intensité des bandes d'absorption des ligands libres quand ceux-ci sont coordonnés à l'ion Tl(III). Dans quelques cas on a mis en évidence aussi de nouvelles bandes d'absorption en ultra-violet (UV) ou visible.

En ce qui concerne les caractéristiques spectrales des ligands en UV et visible, on peut remarquer la présence des bandes d'absorption qui correspondent aux transitions de type $\pi-\pi^*$ et $n-\pi^*$, le dernier type étant généré par des transitions électroniques d'une orbitale nonliante de l'atome d'azote donneur, en état de hybridation sp^2 , sur l'orbitale antiliante π^* . Les transitions $\pi-\pi^*$, qui sont aussi possibles, apparaissent à des longueurs d'onde plus basses, dans l'UV éloigné, et elles ne seront pas prises en considération.

Ainsi, le thiazol et ses dérivés [8] présentent en UV deux bandes d'absorption situées à 210...216 nm ($n-\pi^*$) respectivement 250...260 nm ($\pi-\pi^*$), la position des maxima d'absorption étant en fonction de la nature des groupements greffés sur le noyau thiazolique. Le benzthiazol présente aussi une troisième bande, à $\lambda_{\text{max}} = 287$ nm, qui correspond à une transition $\pi-\pi^*$. Dans les spectres des complexes thalliques correspondants, $\text{TlX}_3 \cdot 2\text{ABT}$ et $\text{TlX}_3 \cdot 2\text{BT}$, en UV, les bandes des ligands libres se retrouvent déplacées par des effets bathochromes ou hipssochromes.

Les spectres électroniques des complexes mentionnés ci-dessus sont présentés dans la Fig. 1. On observe que les bandes du ligand ABT avec les maxima situées à 216 nm et 257 nm sont retrouvées à 210 nm, respectivement 247 nm (pour les complexes avec $\text{X}=\text{Cl}$), comme conséquence de la diminution de la densité électronique de l'atome d'azote donneur à la suite de la réaction avec TlX_3 . En outre, dans les spectres des combinaisons complexes $\text{TlX}_3 \cdot 2\text{ABT}$ apparaît, en spectre visible, une nouvelle bande d'absorption avec $\lambda_{\text{max}} = 416$ nm ($\text{X} = \text{Cl}$), respectivement $\lambda_{\text{max}} = 414$ nm ($\text{X} = \text{Br}$). Nous considérons que ces bandes sont dues à un transfert de charge ligand $\rightarrow$ métal et sont caractéristiques aux complexes formés. Par surcroît on constate que leurs maxima se déplacent par des effets hipssochromes avec l'augmentation de la polarité du solvant. L'explication doit être corrélée avec la modification de l'énergie nécessaire de l'apparition du transfert de charge intermoléculaire qui augmente avec l'accroisse-

ment de la polarité du solvant qui suit l'ordre : alcool éthylique < acé-
tone < acétonitrile.

De telles considérations sont valables même dans les cas des complexes
thalliques avec quinoxaline, ($\text{TIX}_3 \cdot 2\text{QUIN}$). Compte tenu que la dispo-

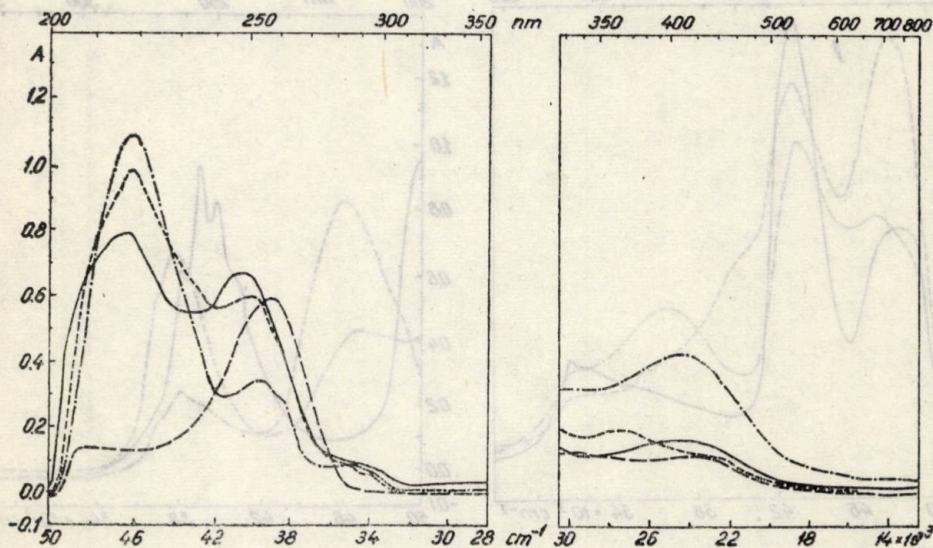


Fig. 1. — Spectres d'absorption électronique : a) en ultra-violet : — $\text{TiCl}_3 \cdot 2\text{ABT}$, $C = 1 \cdot 10^{-4} \text{ M}$; — $\text{TiCl}_3 \cdot 2\text{BT}$, $C = 1,2 \cdot 10^{-5} \text{ M}$; — ABT , $C = 1 \cdot 10^{-4} \text{ M}$; — BT , $C = 0,5 \cdot 10^{-4} \text{ M}$; solvant : alcool éthylique; b) en visible : — $\text{TiCl}_3 \cdot 2\text{ABT}$, $C = 1,5 \cdot 10^{-4} \text{ M}$, solvant : alcool éthylique; — $\text{TiCl}_3 \cdot 2\text{ABT}$, $C = 1,5 \cdot 10^{-4} \text{ M}$, solvant : acéto-
ne; — $\text{TiCl}_3 \cdot 2\text{ABT}$, $C = 3 \cdot 10^{-4} \text{ M}$, solvant : alcool éthylique.

nibilité d'électrons des atomes d'azote de la molécule du ligand est beau-
coup plus réduite ($\text{pK}_a = 0,60$), par conséquent les bandes du ligand
libre seront un peu affectées. On observe dans la Fig. 2 que le spectre de la
quinoxaline présente quatre bandes d'absorption avec les maxima situées
à 208 nm ($n-\pi^*$), 233 nm ($n-\pi^*$), 303 nm ($\pi-\pi^*$) et 313 nm ($\pi-\pi^*$) [8].
Dans les spectres des complexes correspondants les quatre bandes se re-
trouvent à des longueurs d'onde approximativement identiques, mais
avec une augmentation de l'intensité d'absorption, en particulier dans
le cas de la première transition $n-\pi^*$, ce qui met en évidence la capacité
 σ -donneuse du ligand par l'atome d'azote. D'autre part, le fait que la
deuxième bande $n-\pi^*$ présente la même intensité que le ligand libre con-
duit à l'hypothèse que le ligand est coordonné par un seul atome d'azote
donneur.

En ce qui concerne les ligands du type des acides pyridin-mono-
carboxyliques, PIC(1,2), NIC (1,3) et INIC (1,4), on mentionne que leurs
spectres contiennent deux bandes d'absorption (Fig. 3). Une première-
bande, avec le maximum situé dans l'intervalle 210...215 nm, associée à
une transition $\pi-\pi^*$ et une deuxième bande, située à 250...270 nm, con-

séquence de la modification de la bande $n-\pi^*$ de la molécule de pyridine grâce au groupement $-\text{COOH}$ des positions 2, 3, 4 dans les molécules des trois acides pyridine-monocarboxyliques. Dans les fig. 4 et 5 on présente

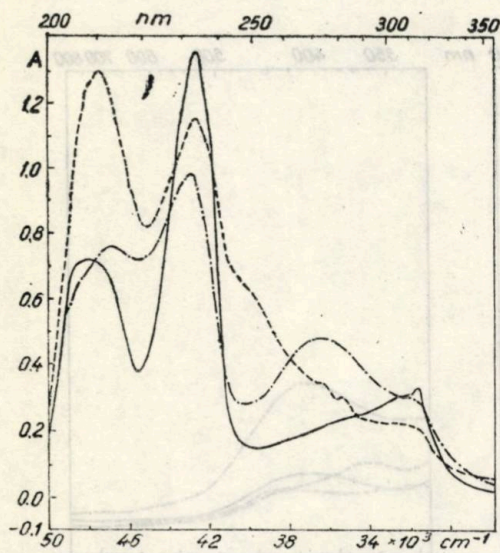


Fig. 2. — Spectres d'absorption électronique : — QUIN, $C = 1 \cdot 10^{-5}$ M, solvant : alcool éthylique ; — $\text{TiCl}_3 \cdot 2\text{QUIN}$, $C = 5 \cdot 10^{-5}$ M, solvant : alcool éthylique ; — $\text{TlBr}_3 \cdot 2\text{QUIN}$, $C = 5 \cdot 10^{-5}$ M, solvant : alcool éthylique.

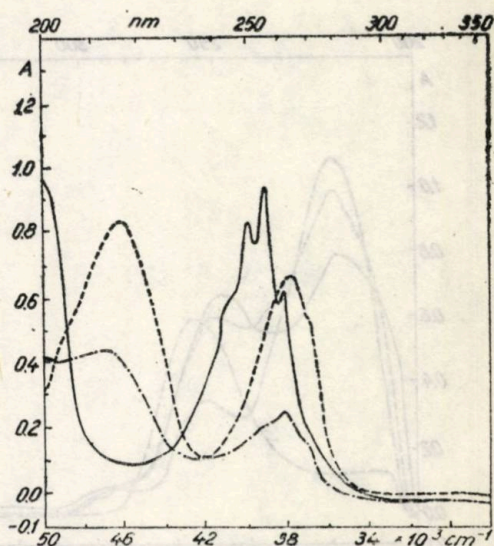


Fig. 3. — Spectres d'absorption électronique : — Pyridine, $C = 5 \cdot 10^{-4}$ M ; — PIC, $C = 1 \cdot 10^{-3}$ M, — NIC, $C = 2 \cdot 10^{-4}$ M, solvant : alcool éthylique.

les spectres des complexes thalliques avec les ligands PIC, NIC et INIC. Les spectres indiquent des modifications des deux bandes. Ainsi, pour les complexes $\text{TlX}_3 \cdot 2\text{PIC}$, la première bande est supprimée, mais la deuxième est déplacée à 267 nm ($\text{X}=\text{Cl}$), en indiquant que la coordination du ligand implique tant le groupement $-\text{COOH}$ aussi que l'atome d'azote de l'hétérocycle ; la formation des chélates est donc très probable. Pour les complexes avec les ligands NIC et INIC les spectres électroniques indiquent seulement la coordination par l'atome d'azote et donc la formation des chélates est impossible.

L'étude des spectres électroniques met aussi en évidence la formation et la structure probable des complexes du Tl(III) avec le ligand ADIP. On peut mentionner que le ligand préparé selon une recette trouvée dans la littérature [9] a été obtenu dans la forme *trans*. En effet son spectre électronique contient trois bandes d'absorption, ce qu'on peut observer dans la Fig. 6. La première bande correspond à une transition $\pi-\pi^*$ localisée au noyaux pyridiniques avec $\lambda_{\text{max}} = 225$ nm, relativement intense, la deuxième ($\pi-\pi^*$) caractéristique à la molécule entière de ligand ($\lambda_{\text{max}} = 313$ nm) et la troisième ($n-\pi^*$) avec $\lambda_{\text{max}} = 455$ nm. La forme *cis* du même ligand ne présente pas la troisième bande.

Les spectres des complexes sont dominés par les trois bandes du ligand libre avec les modifications concernant leur position et l'intensité. Une première conclusion est celle que dans les molécules des complexes

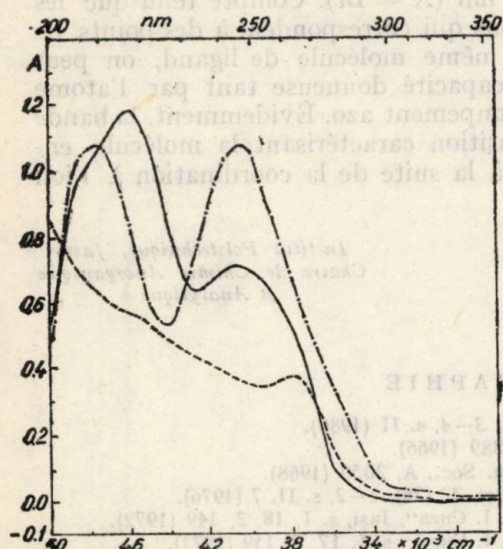


Fig. 4. — Spectres d'absorption électronique :
— $\text{TiCl}_3 \cdot 3\text{NIC}$, $C = 0,5 \cdot 10^{-5} \text{ M}$; — $\text{TiCl}_3 \cdot 2\text{PIC}$, $C = 0,5 \cdot 10^{-5} \text{ M}$; — $\text{TiCl}_3 \cdot 3\text{NIC}$, $C = 1 \cdot 10^{-4} \text{ M}$; solvant : alcool éthylique.

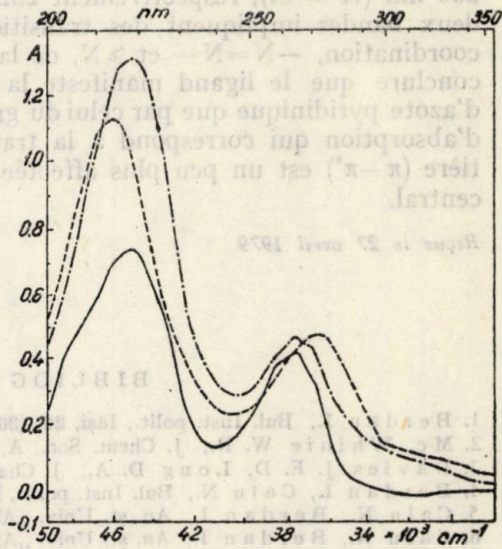


Fig. 5. — Spectres d'absorption électronique :
— $\text{TiBr}_3 \cdot 2\text{PIC}$, $C = 0,5 \cdot 10^{-5} \text{ M}$; — $\text{TiBr}_3 \cdot 3\text{NIC}$, $C = 1 \cdot 10^{-4} \text{ M}$; solvant : alcool éthylique.

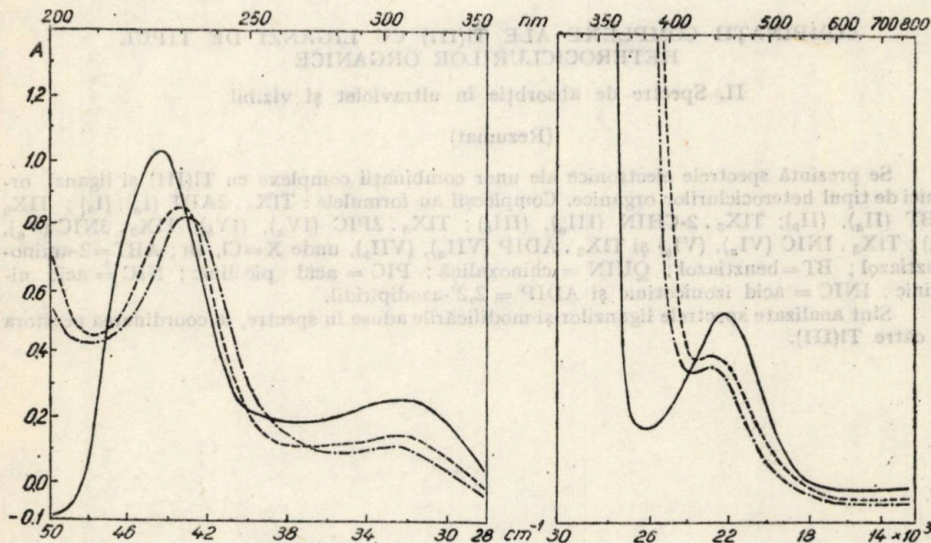


Fig. 6. — Spectres d'absorption électronique : a) en ultra-violet : — ADIP ;
— $\text{TiCl}_3 \cdot \text{ADIP}$, $C = 1 \cdot 10^{-4} \text{ M}$, solvant : alcool éthylique ; — $\text{TiBr}_3 \cdot \text{ADIP}$; b) en
visible : $C = 1 \cdot 10^{-2} \text{ M}$, cuve : 0,5 cm.

TiX_3 . ADIP, le ligand garde la forme *trans*. D'autre part, la bande $n-\pi^*$ avec $\lambda_{max} = 455$ nm est déplacée à 450 nm ($X=Cl$) respectivement 451 nm ($X=Br$). De même, la bande $\pi-\pi^*$, avec $\lambda_{max} = 225$ nm est déplacée à 230 nm ($X=Cl$), respectivement 232 nm ($X=Br$). Compte tenu que les deux bandes impliquent des transitions qui correspondent à des points de coordination, $-N=N-$ et $\geq N$, de la même molécule de ligand, on peut conclure que le ligand manifeste la capacité donneuse tant par l'atome d'azote pyridinique que par celui du groupement azo. Évidemment, la bande d'absorption qui correspond à la transition caractérisant la molécule entière ($\pi-\pi^*$) est un peu plus affectée à la suite de la coordination à l'ion central.

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COMBINAȚII COMPLEXE ALE $Ti(III)$ CU LIGANZI DE TIPUL HETEROCICLURILOR ORGANICE

II. Spectre de absorbție în ultraviolet și vizibil

(Rezumat)

Se prezintă spectrele electronice ale unor combinații complexe cu $Ti(III)$ și liganzi organici de tipul heterociclorilor organice. Complecșii au formulele: $TiX_3 \cdot 2ABT$ (I_a), (I_b); $TiX_3 \cdot 2BT$ (II_a), (II_b); $TiX_3 \cdot 2CHIN$ (III_a), (III_b); $TiX_3 \cdot 2PIC$ (IV_a), (IV_b); $TiX_3 \cdot 3NIC$ (V_a), (V_b); $TiX_3 \cdot INIC$ (VI_a), (VI_b) și $TiX_3 \cdot ADIP$ (VII_a), (VII_b), unde $X=Cl, Br$; $ABT=2$ -aminobenzotiazol; $BT=$ benzotiazol; $QUIN=$ chinoxalină; $PIC=$ acid picolinic; $NIC=$ acid nicotinic; $INIC=$ acid izonicotinic și $ADIP=2,2'$ -azodipiridil.

Sînt analizate spectrele liganzilor și modificările aduse în spectre, la coordinarea acestora de către $Ti(III)$.

ELECTROD MEMBRANĂ H^+ , SENSOR ÎN STARE LICHIDĂ PENTRU TITRAREA POTENȚIOMETRICĂ A UNOR ACIZI, BAZE ȘI SĂRURI CU HIDROLIZĂ BAZICĂ (II)

DE

AL. DUCA, ILIE NIȚU ȘI FLORICICA MATEI

1. Introducere

Într-o lucrare anterioară [1] s-a arătat posibilitatea titrării potențimetrice cu baze tari a unor acizi anorganici tari și a unor acizi organici cu constantă de disociere de ordinul 10^{-5} ... 10^{-6} de concentrații cuprinse între 10^{-1} ... 10^{-4} M.

În lucrarea de față sînt prezentate atît datele experimentale obținute la titrarea potențimetrică a unor baze tari, baze slabe și a unor săruri cu hidroliză bazică folosind aceeași membrană lichidă ca electrod ion-sensor (indicator), același lanț electrochimic și aceeași aparatură pentru măsurarea potențialului de membrană, cît și o interpretare teoretică a funcționării electrodului membrană H^+ -sensor.

2. Rezultate și discuții

Aparatura și modul de lucru fiind descrise în lucrarea anterioară [1] se vor da rezultatele obținute în cazul titrării potențimetrice a unor baze și săruri cu hidroliză bazică. În fig. 1 sînt prezentate curbele de titrare potențimetrică a unor soluții de KOH de concentrații 10^{-1} ... 10^{-3} M.

În fig. 2 sînt reprezentate curbele de titrare potențimetrică a unor baze slabe, ca NH_4OH , $N(C_2H_4OH)_3$ și $NH(C_2H_5)_2$, de concentrații 10^{-1} ... 10^{-3} M, cu soluții de HCl 1 M, 10^{-1} M și 10^{-2} M.

Curbele de titrare potențimetrică a unor săruri cu hidroliză bazică de concentrații 10^{-1} ... 10^{-3} M, cu soluții de HCl 1 M, 10^{-1} M și respectiv 10^{-2} M, sînt redade în fig. 3 și 4.

În fig. 5 sînt reprezentate curbele de titrare potențimetrică ale acidului acetic, de concentrație 10^{-1} ... 10^{-3} M, în prezența unui exces de KOH, cu soluții 1 M, 10^{-1} M și 10^{-2} M de HCl.

Titrarea acidului acetic în prezența unui exces de KOH a fost impusă de faptul că acidul acetic prezintă o constantă de repartiție mult mai mare în raport cu ceilalți acizi ($K = 1,1$).

Din analiza fig. 1...5 se pot face următoarele constatări:

a) Curbele de titrare menționate mai sus, obținute cu electrodul ion-sensor H^+ , au o formă diferită de cele obținute prin potențimetrie clasică, excepție făcând curba obținută la titrarea KOH cu H_2SO_4 , ca urmare a faptului că H_2SO_4 se repartizează puțin și în faza organică.

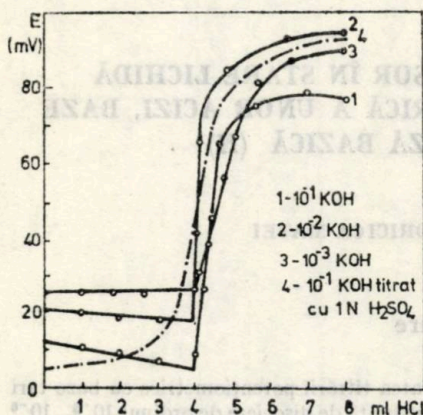


Fig. 1. — Curbele de titrare potențimetrică a KOH de diferite concentrații: 1 — sol. 10^{-1} M KOH; 2 — sol. 10^{-2} M KOH; 3 — sol. 10^{-3} M KOH titrate cu HCl 1 M, 10^{-1} M și 10^{-2} M; 4 — sol. 10^{-1} M KOH titrată cu sol. 1 M H_2SO_4 .

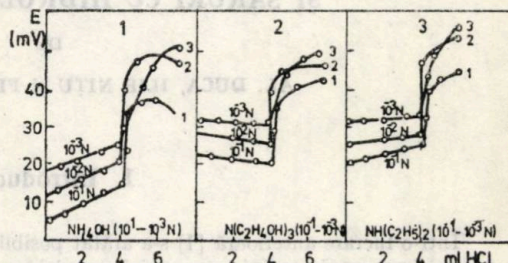


Fig. 2. — Curbele de titrare ale unor baze slabe de diferite concentrații: 1 — sol. 10^{-1} ... 10^{-3} M NH_4OH ; 2 — sol. 10^{-1} ... 10^{-3} M $N(C_2H_5OH)_3$; 3 — sol. 10^{-1} ... 10^{-3} M $NH(C_2H_5)_2$.

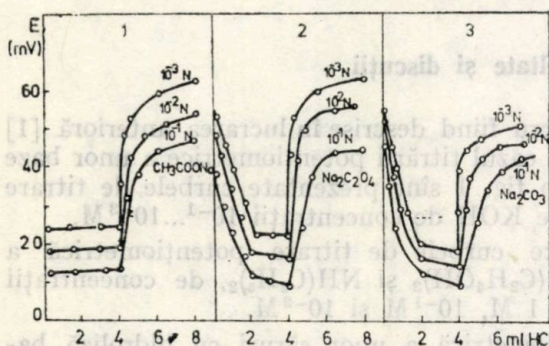


Fig. 3. — Curbele de titrare potențimetrică a unor săruri cu hidroliză bazică: 1 — sol. 10^{-1} ... 10^{-3} M CH_3COONa ; 2 — sol. 10^{-1} ... 10^{-3} M $Na_2C_2O_4$; 3 — sol. 10^{-1} ... 10^{-3} M Na_2CO_3 .

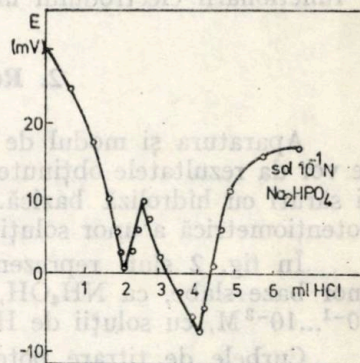


Fig. 4. — Curba de titrare a unei soluții 10^{-1} M Na_2HPO_4 cu o soluție 1 M HCl.

b) Curbele de titrare potențimetrică a sărurilor cu hidroliză bazică provenite din acizi bibazici pun în evidență ambele puncte de echivalență.

c) Curba de titrare potențimetrică a soluțiilor de fosfat disodic se caracterizează prin două valori de minim și una de maxim. Valorile de minim corespund celor două puncte de echivalență.

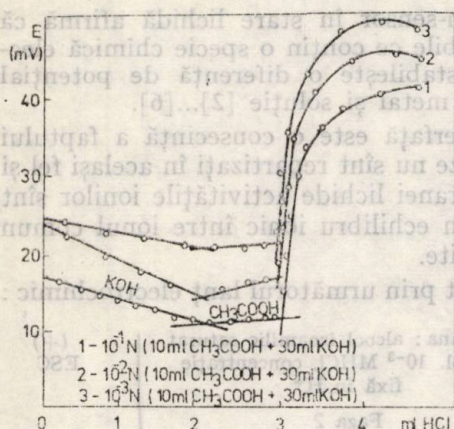


Fig. 5. — Curbele de titrare potențimetrică ale acidului acetic cu soluții de HCl 1 M...
... 10^{-2} M: 1 — 10 ml sol. 10^{-1} M CH_3COOH + 30 ml sol. 10^{-1} M KOH; 2 — 10 ml sol. 10^{-2} M CH_3COOH + 30 ml sol. 10^{-2} M KOH; 3 — 10 ml sol. 10^{-3} M CH_3COOH + 30 ml sol. 10^{-3} M KOH.

d) Curba de titrare a acidului acetic, în cazul în care se folosește un exces de KOH, pune în evidență și punctul de echivalență corespunzător excesului de KOH.

e) Punctele de echivalență se localizează net pînă la concentrații 10^{-3} M, dar modul de localizare diferă la unele săruri cu hidroliză bazică (de exemplu la Na_2HPO_4).

f) Pentru concentrații mai mici decît 10^{-3} M localizarea punctului de echivalență este posibilă numai prin interpolare.

Tabelul 1

Bazele și sărurile cu hidroliză bazică folosite (40 ml sol. 0,1 N)	Volumul de soluție 1 N de HCl consumat la titrare cm^3	
	Metoda cu electrod ion-sensor	Metoda conductometrică
KOH	4,06	4,04
NH_4OH	3,96	3,95
NaCOOCH_3	4,05	4,01
Na_2CO_3	4,02	3,98
$\text{Na}_2\text{C}_2\text{O}_4$	4,04	4,02
Na_2HPO_4	4,06	4,04

g) Saltul de potențial din jurul punctului de echivalență este satisfăcător (aproximativ 40 mV).

b) În tabelul 1 sînt redată comparativ rezultatele obținute la titrarea unor baze și săruri cu hidroliză bazică de concentrații 0,1 M cu o soluție 1 M HCl prin metoda conductometrică și metoda cu electrod ion-sensor.

3. Principiul de funcționare al electrozilor ion-sensor membrană lichidă

Teoria electrozilor membrană ion-sensor în stare lichidă afirmă că la interfața a două faze lichide nemiscibile ce conțin o specie chimică electroactivă în concentrații diferite, se stabilește o diferență de potențial la fel ca și în cazul interfețelor dintre metal și soluție [2]...[6].

Apariția acestui potențial de interfață este o consecință a faptului că ionii speciei chimice din cele două faze nu sînt repartizați în același fel și ca urmare pe cele două fețe ale membranei lichide activitățile ionilor sînt diferite stabilindu-se de fiecare dată un echilibru ionic între ionul comun prezent în cele două faze lichide diferite.

Electrodul ion-sensor poate fi redat prin următorul lanț electrochimic :

(+) ESC	Soluție apoasă de concentrație variabilă în H^+	Membrana : alcool izoamilic saturat în sol. 10^{-3} M HCl, concentrație fixă în H^+	(+) ESC
	Faza 1	Faza 2	

Dacă fazele 1 și 2 se găsesc în echilibru electrochimic, atunci potențialele electrochimice ale ionilor de H^+ în cele două faze sînt egale

$$(1) \quad \bar{\mu}_{H^+_{(1)}} = \bar{\mu}_{H^+_{(2)}}$$

Potențialul electrochimic al speciei chimice H^+ , pentru cele două faze, are următoarele expresii :

$$(2) \quad \bar{\mu}_{H^+_{(1)}} = \mu_{H^+_{(1)}} + Z_H + F\varphi_{(1)}, \quad (3) \quad \bar{\mu}_{H^+_{(2)}} = \mu_{H^+_{(2)}} + Z_H + F\varphi_{(2)}$$

Potențialul chimic al ionilor H^+ din faza apoasă (1) are expresia :

$$(4) \quad \mu_{H^+_{(1)}} = \mu_{H^+_{(1)}}^0 + RT \ln a_{H^+_{(1)}}$$

Din relațiile (1)...(3) rezultă :

$$(5) \quad \mu_{H^+_{(2)}} + Z_H + F\varphi_{(2)} = \mu_{H^+_{(1)}}^0 + RT \ln a_{H^+_{(1)}} + Z_H + F\varphi_{(1)}$$

încît

$$(6) \quad \varphi_{(2)} - \varphi_{(1)} = \frac{\mu_{H^+_{(1)}}^0 - \mu_{H^+_{(2)}}}{Z_H + F} + \frac{RT}{Z_H + F} \ln a_{H^+_{(1)}}$$

Dacă activitatea ionilor H^+ din faza 2 este independentă de activitatea ionilor H^+ din faza 1 (condiție satisfăcută în cazul cînd constanta de repartitie a ionilor H^+ dintre cele două faze este foarte mare), atunci $\mu_{H^+_{(2)}} = \text{const.}$ și relația (6) devine :

$$(7) \quad \varphi_{(2)} - \varphi_{(1)} = \varepsilon^0 + \frac{RT}{Z_H + F} \ln a_{H^+_{(1)}}$$

Diferența $\varphi_{(2)} - \varphi_{(1)}$ reprezintă potențialul de membrană pe care îl notăm cu ϵ . Astfel, relația (7) devine:

$$(8) \quad \epsilon = \epsilon^0 + \frac{RT}{Z_H + F} \ln a_{H^+_{(1)}} \quad (17)$$

sau:

$$(9) \quad \epsilon = \epsilon^0 + 0,058 \log a_{H^+_{(1)}}, \quad Z_{H^+} = 1.$$

Mărimile din relațiile (1)...(9) au următoarele semnificații: $\mu_{H^+_{(1)}}^0$ — potențialul chimic standard al ionilor de hidrogen; $\varphi_{(1)}$ și $\varphi_{(2)}$ — potențialele electrice interne ale fazelor 1 și 2; R — constanta universală a gazelor; T — temperatura absolută; $F = 96\,500$ C constanta lui Faraday; ϵ^0 — independent de a_{H^+} și cuprinde atât potențiale de contact între membrană și electrozii de referință cât și potențialul datorat tensiunilor de asimetrie ce apar pe cele două suprafețe ale membranei.

În definitiv se poate scrie relația:

$$\epsilon^0 = \epsilon^{0'} + \epsilon_{\text{contact}} + \epsilon_{\text{asim}}.$$

3. 1. Selectivitatea electrozilor cu membrană lichidă

Pentru ca potențialul de membrană să respecte relația lui Nernst este necesar ca electrodul ion-sensor să îndeplinească următoarele condiții: a) ionul H^+ să nu se transfere din faza 1 în faza 2 atunci când fazele vin în contact; b) faza 2 să posede proprietăți conductoare, adică să aibă un potențial electric interior de fază.

Aceste două condiții asigură funcționarea electrodului conform relației lui Nernst numai pentru ionii H^+ . Prezența altor ioni în soluție duce adeseori la o modificare a potențialului de membrană.

Electrodul membrană H^+ -sensor devine selectiv (specific) pentru H^+ numai dacă prezența altor ioni în soluție nu influențează potențialul de membrană.

Dacă se consideră că membrana lichidă specifică pentru ionul de hidrogen este în contact cu o soluție care conține pe lângă ionul H^+ și ioni de Na^+ , K , NH_4 , Mg , Ca etc., atunci între cele două faze se stabilește un echilibru ionic iar potențialele electrochimice ale ionilor de H^+ și Na^+ din cele două faze devin egale:

$$(10) \quad H^+_{(2)} + Na^+_{(1)} = H^+_{(1)} + Na^+_{(2)}$$

sau în general:

$$(11) \quad i_{(2)} + j_{(1)} = i_{(1)} + j_{(2)}.$$

Conform relației (5) se poate scrie:

$$(12) \quad \mu_{H^+_{(2)}}^0 + RT \ln a_{H^+_{(2)}} + F\varphi_{(2)} = \mu_{H^+_{(1)}}^0 + RT \ln a_{H^+_{(1)}} + F\varphi_{(1)}$$

și:

$$(13) \quad \mu_{Na^+_{(2)}}^0 + RT \ln a_{Na^+_{(2)}} + F\varphi_{(2)} = \mu_{Na^+_{(1)}}^0 + RT \ln a_{Na^+_{(1)}} + F\varphi_{(1)}.$$

Din relațiile (12) și (13) rezultă :

$$(14) \quad \left[\frac{a_{H^+}^{(1)}}{a_{H^+}^{(2)}} \right] \left[\frac{a_{Na^+}^{(2)}}{a_{Na^+}^{(1)}} \right] = \exp \left[\frac{A_{Na^+}^0 - A_{H^+}^0}{RT} \right] = K_{H^+/Na^+}, \quad (8)$$

în care $A_{H^+}^0$ și $A_{Na^+}^0$ sînt potențialele chimice standard de transfer ale ionilor H^+ și Na^+ din faza 1 în faza 2, exprimate prin relațiile :

$$(15) \quad A_{H^+}^0 = \mu_{H^+}^0 - \mu_{H^+}^0, \quad A_{Na^+}^0 = \mu_{Na^+}^0 - \mu_{Na^+}^0.$$

Condiția de selectivitate a membranei H^+ pentru ionii H^+ este dată de inegalitatea :

$$(16) \quad A_{Na^+}^0 \ll A_{H^+}^0 \text{ sau în general } A_j^0 \ll A_i^0.$$

Dacă această condiție nu este respectată, din relațiile (14) și (15) se poate deduce expresia potențialului de membrană a electrodului membrană H^+ -sensor pentru ionii H^+ întrucît un alt ion (Na^+) prezent în soluția de analizat modifică potențialul de membrană :

$$(17) \quad \epsilon = \epsilon^0 + \frac{RT}{F} \ln (a_{H^+} + K_{H^+/Na^+} a_{Na^+}).$$

Potențialul de membrană specific pentru un ion i , în prezența mai multor ioni care interferă ($j=n-1$), este dat de expresia :

$$(18) \quad \epsilon = \epsilon^0 + \frac{RT}{ZF} \ln (a_i + K_{i/j} a_j^{z_i/z_j}),$$

mărimea $K_{i/j}$ (K_{H^+/Na^+}) reprezentînd constanta de selectivitate; din valoarea acesteia se poate aprecia în ce măsură ionii interferenți (j) afectează potențialul de membrană.

Cu cît constanta de selectivitate are valori mai mici cu atît electrodul ion-sensor devine mai selectiv.

4. Concluzii

1. Electrodul membranei H^+ -sensor poate fi utilizat cu rezultate bune în titrarea unor baze tari și slabe precum și în titrarea unor săruri cu hidroliză bazică în domeniul de concentrație $10^{-1} \dots 10^{-4}$ M.

2. Saltul de potențial în jurul punctului de echivalență este satisfăcător.

3. Precizia titrărilor efectuate cu electrodul membrană H^+ -sensor este comparabilă cu precizia determinărilor conductometrice (cîteva rezultate fiind redate în tabelul 1).

4. S-a elaborat o interpretare teoretică a funcționării electrodului membrană H^+ -sensor în stare lichidă.

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H⁺-MEMBRANE ELECTRODE AS A LIQUID SENSOR FOR THE POTENTIOMETRIC TITRATION OF SOME ACIDES, BASES AND SALTS WITH BASIC HYDROLYSIS (II)

(Summary)

The obtaining of the interface between the isoamylic solution saturated with 10^{-3} M HCl and the test solution (with variable H^+ concentration) as an H^+ -membrane electrode sensor in potentiometric titration of some bases of different strengths and of some salts with basic hydrolysis is studied.

KOMPLEXE VERBINDUNGEN VON NEUTRALROT (3-AMINE-6-DIMETHYLAMINE-2-METHYLPHENAZIN)

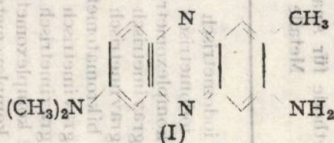
VON

SIMON FIȘEL und LUMINIȚA PĂUNESCU

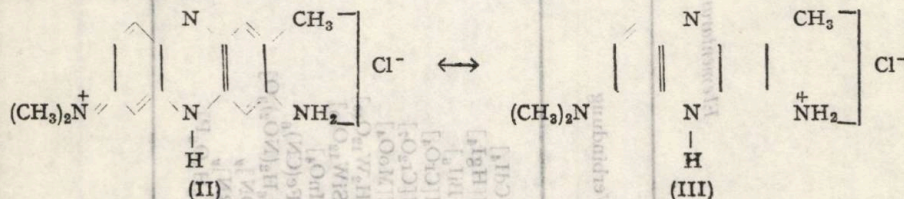
Phenazin Verbindungen mit Metallionen (Bi, Pd, Cd, Hg, Cu) wurden das Erstemal, schon 1933, von Pavolini beschrieben [1]. Andere Untersuchungen über die Bildung von metallischen Komplexen mit Phenazinenderivaten [2]...[7] beziehen sich auf den Gebrauch dieser Komplexe in der analytischen Chemie, [1], [8]...[10], für die Stabilisierung von ungewöhnlichen Valenzzuständen der Metalle [11], [12] und für Arzneimittel [13]... [18].

Im allgemein wird das Neutralrot (N.R.) in Form eines Chlorhydrats angetroffen. Die Verbindung, ohne Substitution des aminischen Wasserstoffes mit der Methylgruppe war das Forschungsobjekt von Clark und Perkins [19], wogegen die mit Methylgruppen substituierten Verbindungen von Mayer und seinem Mitarbeitern [20] untersucht wurden sind. Nikolski und seine Mitarbeitern beschäftigten sich mit dem Gleichgewicht zwischen Neutralrot und seiner Leuco-Form, sowie mit dem Zwischenprodukt welches bei pH = 4...6 angetroffen wird [21].

In gegenwärtiger Arbeit werden einige Nachweisreaktionen des Neutralrots folgender Struktur:



beschrieben, welches in Gegenwart von Salzsäure ein Chlorhydrat chinoidischer Struktur bildet:



2. Experimenteller Teil

Es wurden die entsprechende Verbindungen mit $[\text{HgI}_4]^{2-}$, $[\text{BiI}_6]^{3-}$, $[\text{MoO}_4]^{2-}$, $[\text{CdI}_4]^{2-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{MnO}_4]^-$, $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, $[\text{C}_3\text{H}_5\text{O}_6\text{P}]^-$, $[\text{CrO}_4]^{2-}$, $[\text{Cr}_2\text{O}_7]^{2-}$, Pikrinsäure (PS), Deoxiribonukleinsäure (ADN), Ribonukleinsäure (ARN) synthetisiert. Dabei wurden 10^{-1} M

Tabelle 1
 Elementaranalyse von Komplexverbindungen des Neutraltrots (Mittel von 3 Bestimmungen, Fehler Grenze $\pm 0,5\%$)

Nr.	Verbindung	Methode für Analyse der Metalle	Metalle		N		C		H	
			Berechn.	Gefunden	Berechn.	Gefunden	Berechn.	Gefunden	Berechn.	Gefunden
			%	%	%	%	%	%	%	%
1	$[\text{R.N.H}]_2 [\text{CdI}_4]$	Cd iodometrisch	9,97	9,65	9,94	9,45	31,98	33,44	3,04	3,66
2	$[\text{R.N.H}]_2 [\text{HgI}_4]$	Hg iodometrisch	20,84	20,29	5,82	5,75	48,71	48,64	1,88	1,96
3	$[\text{R.N.H}]_3 [\text{BiI}_6]$	Bi komplexometrisch	12,07	11,48	9,71	9,32	31,23	31,16	2,97	3,02
4	$[\text{R.N.H}]_3 [\text{CrO}_4]$	Cr gravimetrisch	14,04	13,89	15,12	14,69	48,64	49,20	4,89	5,02
5	$[\text{R.N.H}]_3 [\text{CrO}_4]$	Cr gravimetrisch	22,11	22,80	11,91	12,14	38,30	38,78	3,85	3,35
6	$[\text{R.N.H}]_3 [\text{MoO}_4]$	Mo bikromatometrisch	23,15	22,89	13,52	13,21	43,48	43,21	4,37	4,10
7	$[\text{R.N.H}]_6 [\text{H}_2\text{W}_{12}\text{O}_{40}]$	W gravimetrisch	50,51	50,25	7,69	7,20	24,74	24,32	2,35	2,67
8	$[\text{R.N.H}]_4 [\text{SiW}_{12}\text{O}_{40}]$	W gravimetrisch	56,75	56,80	5,76	5,36	18,53	18,90	1,76	1,66
9	$[\text{R.N.H}]_3 [\text{MnO}_4]$	Mn komplexometrisch	14,75	15,05	15,05	15,12	48,39	48,06	4,60	4,27
10	$[\text{R.N.H}]_3 [\text{Fe(CN)}_6]$	Fe komplexometrisch	5,74	5,61	25,94	25,97	63,02	63,12	5,28	5,29
11	$[\text{R.N.H}]_3 [\text{C}_6\text{H}_5(\text{NO}_2)_3\text{O}]$				20,36	16,37	52,39	50,30	3,97	3,51
12	$[\text{R.N.}]_2 [\text{ADN}]_2$				13,20	15,61		36,53		3,54
13	$[\text{R.N.}]_2 [\text{ARN}]_2$					13,78		35,53		3,16
14	$[\text{R.N.H}]_2 [\text{C}_3\text{H}_8\text{O}_6\text{P}]$						50,94	50,90	5,93	5,40

wässrige Lösungen benutzt ($K_2[HgI_4]$, $K_3[BiI_6]$, $(NH_4)_2MoO_4$, K_2CrO_4 , $K_2[CdI_4]$, $K_3[Fe(CN)_6]$, $KMnO_4$, $H_6[H_2W_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, $K_2Cr_2O_7$, Pikrinsäure (PS), $C_3H_8O_6PNa$, ADN, ARN). Das Reaktionsmedium war Salzsäure von maximal $pH=1$, mit Ausnahme von Desoxiribonuclein- und Ribonucleinsäure, für welche die Reaktion bei $pH=6\ldots 7$ durchgeführt wurde.

Die gebildeten Niederschläge wurden filtriert mit Wasser und anschliessend mit wenig Alkohol und mit sehr wenig Äther gewaschen. Die erhaltenen Verbindungen wurden dann im Vakuum bei Zimmertemperatur getrocknet.

Die Ergebnisse der Elementaranalyse der Verbindungen sind in Tabelle 1 wiedergegeben.

Die Ergebnisse der Analysen stimmen mit den berechneten Werten überein und bestätigen somit das Kombinationsverhältniss der gebildeten Komplexe Phenazinderivat — Komplexierungsanion.

Die erhaltenen Verbindungen sind in Wasser, Chloroform, Äzeton, Benzol, Nitrobenzol, Isopropylalkohol, Butylalkohol, Butylazetat unlöslich, teilweise in 1,2 Dichloräthan, Äthylalkohol, Äthyläther, Methyl Äthylketon und Propylänglykohl, in Dimethylsulfoxid, Dimethylformamid und Dioxan, löslich.

Um die Natur der gebildeten Verbindungen zu bestimmen, wurden IR-Analysen an einem Perkin-Elmer 577 Spektrophotometer ($200\ldots 4000\text{ cm}^{-1}$) und einem Spekord 71 Zeiss ($700\ldots 4000\text{ cm}^{-1}$) durchgeführt, wobei KBr-Tabletten benutzt wurden. Die erzielten Daten sind in Tabelle 2 wiedergegeben.

Die UV—VIS Spektren wurden an einen Unicam-Spektrophotometer SP-800 B, sowie auch an einem Spektrophotometer Zeiss-Spekord UV—VIS aufgeglichen. Als Lösungsmittel wurde Dioxan verwendet. Die Absorptionsmaxima, sowie entsprechende Schultern (in Klammern) sind in der Tabelle 3 wiedergegeben.

3. Diskussion der Ergebnisse

Die wesentlichen Prinzipien der IR-Spektroskopie für Heteroatomverbindungen mit 5...6 Gliederkernen sind von Katritzki [23] zusammengefaßt, wogegen die der Chinoline und Isochinoline, die viele Ähnlichkeiten mit dem Phenazinen aufweisen, von Bellamy gedeutet wurden [24].

Das Butylphenazinspektrum wurde von Teuber und Steiger [25] publiziert. Gagnon und Mitarbeitern [26] haben das Spektrum des festen Phenazin im Gebiet $1650\ldots 650\text{ cm}^{-1}$ veröffentlicht. Stammer und Taurins [27] haben bei der Untersuchung des festen Zustandes im Gebiet $4000\ldots 1650\text{ cm}^{-1}$, die Existenz einiger schwachen, wogegen in Tetrachlorkohlenstoff oder Schwefelkohlenstoff von stärkeren Absorptionsbanden aufgezeigt.

Aus den Angaben in Tabelle 2 wird die Gegenwart von charakteristischen Banden für Phenazin in allen untersuchten Verbindungen sowie Verschiebungen der charakteristischen Banden der verwendeten Komplexverbindungen und der typischen Metall—Stickstoff Bindungen festgestellt. Wird z.B. die Verbindung zwischen Neutralrot und Chromat in Betracht gezogen, so stellt man fest, daß die charakteristische Bande des CrO_4^{2-} Iones von 348 cm^{-1} , in der Verbindung bei 360 cm^{-1} vorkommt, d.h. daß eine Verschiebung von 12 cm^{-1} sich bemerkbar macht, wogegen die Cr—N Bindung, die in der Literatur [28] bei $466,44\ldots 475\text{ cm}^{-1}$, angegeben ist, bei wellenlänge angetroffen wird (Abb. 1).

Ähnlich verschiebt sich in der Komplexverbindung von Neutralrot mit Pikrinsäure; das kennzeichnende Dublett der Pikrinsäure ($1629, 1608\text{ cm}^{-1}$) gegen $1600\text{--}1610\text{ cm}^{-1}$, in Form einer sehr ausgeprägten Bande; die entsprechenden Banden für $\nu_{\text{As}(\text{NO}_2)} = 1540\text{ cm}^{-1}$ und $\nu_{\text{S}(\text{NO}_2)} = 1350\text{ cm}^{-1}$, verschieben sich nach 1550 bzw. 1360 cm^{-1} . Die für die Pikrinsäure charakteristische Bande von 3080 cm^{-1} erscheint im Komplex bei $3040\text{--}3080\text{ cm}^{-1}$ sehr abgeflacht. Die neue Bande von $3350\text{--}3380\text{ cm}^{-1}$ bestätigt die Gegenwart einer Wasserstoffsbindung (Abb. 2).

Man kann somit, wie auch in der vorhergehenden Veröffentlichungen [29] über das Neutralrot, annehmen, daß diese neu gebildeten Verbindungen, durch Komplexieren mit Ladungsübertragung, ähnlich wie in Ionenassoziationen, entstanden sind.

Zu erwähnen wären hier noch einige Einschränkungen betreffend die Stabilität der Verbindungen mit Quecksilber und Mangan, sowie auch die der erwähnten Nucleinsäuren.

UV-VIS Spektren anderer Phenazine [30], [31] bestätigen die Bildung von Komplexen mit Ladungsübertragung. Wie auch bei den IR-Spektren, wird als Beispiel die Komplexverbindung zwischen Neutralrot und Pikrinsäure besprochen. Das P.S. weist in Dioxan charakteristische Banden bei $262, (287), 340, 420\text{ nm}$, auf wogegen in der Komplexverbin-

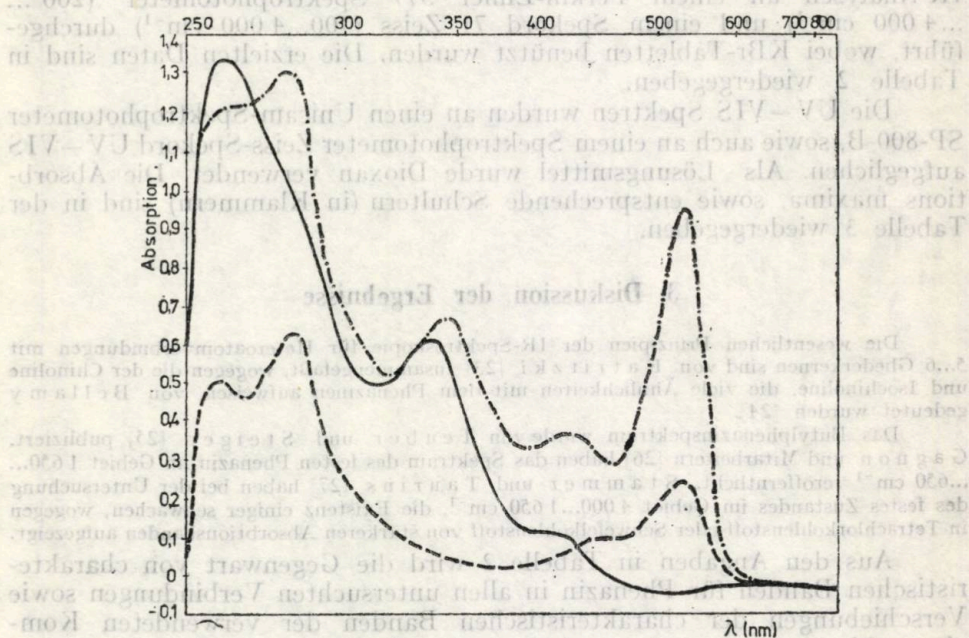


Abb. 3. — UV-VIS Absorptionsspektrum dioxaniger Lösungen von: — PS, - - - [N.R.H] [PS], — NR.

derung bei $(260), 281, 350, 435, 540\text{ nm}$. Die erste Banden können den Elektronensprüngen $\pi_{\text{Zklus}} \rightarrow \pi_{\text{NO}_2}^*$ zugeschrieben werden b.z.w. $\pi_{\text{NO}_2} \rightarrow \pi_{\text{NO}_2}^*$, und die letzte, der intermolekularen Ladungsübertragung, welche für die Komplexbildung charakteristisch ist, d.h. $n_{\text{N}(\text{N.R})} \rightarrow \pi_{\text{NO}_2(\text{P.S})}$ (Abb. 3).

Auch beim Chromatkomplex können Verschiebungen des Kaliumchromatmaximums (255), 277, (357) nm beobachtet werden und zwar nach (261) 282, 520 nm, sowie eine neue Bande für die Bildung des Komplexes (Abb. 4).

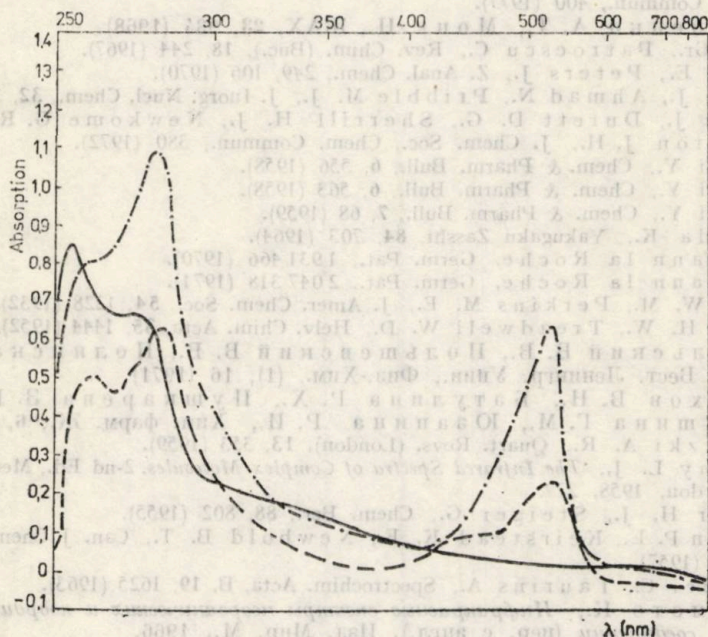


Abb. 4. — UV-VIS Absorptionsspektrum dioxaniger Lösungen von
— K_2CrO_4 , --- $[N.R.H]H[CrO_4]$, - - - NR.

4. Schlußfolgerungen

Vorhergehende Untersuchungen über die Phenazinderivate des ADN [32], [33] sprechen für die Ausbildung von zwei Grundbindungen: eine starke ($K_d = 10^4 \dots 10^6$) und eine schwache ($K_d = 10^3 \dots 10^4$) wobei die Bindung mit Anwachsen der Ionenstärke geschwächt wird. Diese Beobachtung ist im Einklang mit dem Einschachtelungsmodell das für alle Phenazine (planförmige und trizyklisch aromatische Verbindungen). Somit sprechen auch die Ergebnisse der IR, UV-VIS Spektren für die Bildung von Komplexverbindungen durch Landungsübertragung.

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COMPUȘI COMPLECȘI AI ROȘULUI NEUTRU

(3-AMINO-6-DIMETILAMINO-2-METILFENAZINĂ)

(Rezumat)

S-au preparat 14 complecși ai roșului neutru cu $[\text{HgI}_4]^{2-}$, $[\text{BiI}_6]^{3-}$, $[\text{MoO}_4]^{2-}$, $[\text{CdI}_4]^{2-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{MnO}_4]^-$, $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, $[\text{CrO}_4]^{2-}$, $[\text{Cr}_2\text{O}_7]^{2-}$, $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]^-$, ADN, ARN, $[\text{C}_3\text{H}_8\text{O}_6\text{P}]^-$.

Spectrele în domeniul IR, UV și vizibil pledează pentru formarea, prin transfer de sarcină, a unor complecși de tipul asocierilor ionice.

LA SOLVATATION SÉLECTIVE DES RÉSINES ÉCHANGEUSES D'IONS DE TYPE DOWEX 50WX8 DANS DES MÉLANGES ÉTHANOL—EAU

PAR

AL. CECAL

1. Introduction

Le processus de solvation préférentielle des ions simples ou complexés par les molécules de solvant présentes dans le système donné a préoccupé un grand nombre d'auteurs. À cet égard on peut citer Popovych et ses collaborateurs [1]...[3] qui ont initié des études approfondies concernant l'estimation de l'effet du milieu sur certains ions se trouvant dans des combinaisons anorganiques simples, dans des mélanges d'eau—solvants non aqueux (méthanol, éthanol, acétonitrile) et ont proposé de différentes relations qui lient ce paramètre de certaines constantes physiques, à savoir le potentiel standard, la constante sélective etc. Kim et d'autres auteurs [4]...[7] ont étudié la solvation préférentielle des ions singuliers ainsi que des certains cations et anions se trouvant dans des résines échangeuses d'ions, en présence des mélanges eau—solvants organiques (méthanol, éthanol, propanol, butanol, glycol, acétone, acétonitrile, dioxane, etc.) aboutissant à la conclusion que le phénomène respectif est très complexe et que pour obtenir une évaluation analytique il faut avoir en vue les énergies libres standard, les rayons et les volumes des ions solvatés, le nombre de molécules d'eau et de solvant organique se trouvant autour de ces édifices à charge, la constante diélectrique du milieu de réaction, etc.

Les interactions de type solvant—solvate ont été décrites en détail par Coetzee et Ritchie [8] ayant en vue une série de facteurs qui y influencent, à savoir: la nature du solvant, le pH du milieu de réaction, la présence de certains électrolytes, etc.

Dans une série d'ouvrages Parker et ses collaborateurs [9]...[14] ont étudié le processus de solvation des ions en calculant, pour diverses conditions expérimentales, les potentiels chimiques standard, les coefficients d'activité des ions singuliers, les entropies, les potentiels de jonction liquide—liquide pour les solutions d'électrolytes en mélanges de solvants, les constantes d'instabilité de certains complexes possibles à se former etc.

Dans ce qui suit on se propose à déterminer, d'une part, l'effet du milieu sur les cations H^+ , K^+ et UO_2^{2+} se trouvant dans des résines échangeuses d'ions de type Dowex 50WX8 et, d'autre part, à étudier l'influence du milieu donné sur le processus d'échange ionique H^+/K^+ , K^+/UO_2^{2+} et H^+/UO_2^{2+} en divers mélanges d'éthanol—eau.

2. Partie expérimentale

Ayant en vue la préparation pour l'ouvrage des résines échangeuses d'ions de type Dowex 50WX8 (100 mesh) on en a pris une quantité quelconque (250 g) qu'on a introduit, après humectation, dans une colonne en verre. On y fait traiter la résine avec 1 000 ml solution NaOH (2N), 1 000 ml eau et 1 000 ml solution HNO_3 (2N) et puis on procède à un lavage

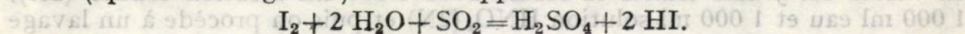
abondant avec de l'eau et du méthanol. Après avoir réalisée une très lente élution de la résine avec 2 000 ml solution de HNO_3 (2N) on extrait la résine de la colonne en verre, on la filtre par un entonnoir Büchner et on la fait laver avec de l'eau jusqu'à ce que le pH du filtrant atteigne le point de neutralité. On fait sécher la résine pendant 24 h, à 130°C et on l'introduit dans un dessiccateur sous vide, rempli de P_2O_5 .

Pour déterminer la capacité de la résine respective sous la forme RH ($5,15 \cdot 10^{-3}$ ions H^+ /g résine sèche) on en a prélevé une quantité de 1 g qu'on a introduit après humectation dans une colonne en verre de dimensions plus réduites. Ensuite on a fait traiter cette portion de résine, antérieurement préparée, avec une quantité connue de solution NaOH (0,1 N) et l'excès de base a été titré avec une solution de HCl (0,1 N).

Pour obtenir des résines échangeuses d'ions sous la forme RK et R_2UO_2 on a fait traiter, séparément, des quantités égales de résine Dowex 50WX8 sous la forme RH, préparée selon les indications ci-dessus, avec des solutions concentrées de KNO_3 et $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. On a répété les éluions jusqu'à ce que l'échange ionique H^+/K^+ et $\text{H}^+/\text{UO}_2^{2+}$ soit réalisé complètement. Ces résines sont lavées avec de l'eau et du méthanol à plusieurs fois, filtrées par des entonnoirs Büchner, séchées et déposées tout comme la résine RH. Pour vérifier si le changement maximum de cations K^+ et UO_2^{2+} des résines correspondentes est atteint, on en prend une quantité de 2 g pour chacune. Ces échantillons sont introduits dans des colonnes en verre et soumis à une élution avec une solution de HNO_3 (2N) pour écarter des résines données les ions de K^+ et UO_2^{2+} et pour les doser séparément. L'ion de potassium a été dosé après précipitation sous la forme de $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$ par titrage avec ZnSO_4 et Complexone III en présence de l'ériochrome T [15], tandis que l'ion d'uranyle a été déterminé gravimétriquement sous la forme de U_3O_8 [16]. Les résultats de ces dosages, effectués avec une erreur sous 5%, ont confirmé le fait que les deux résines ont changé d'ions de K^+ et UO_2^{2+} d'une manière correspondante.

L'étude du processus de solvation sélective des résines échangeuses d'ions de type RH, RK et R_2UO_2 , tout comme l'investigation de l'effet du milieu sur l'échange cationique: H^+/K^+ , $\text{K}^+/\text{UO}_2^{2+}$ et $\text{H}^+/\text{UO}_2^{2+}$ des résines données, a été effectuée en poursuivant les étapes ci-dessous: a) on a préparé des solutions qui contenaient des mélanges éthanol-eau à proportions différentes (fractions molaires); b) on a pesé des quantités à peu près égales (1 g) de résine RH, RK et R_2UO_2 préparées antérieurement, dans des éprouvettes à couvercle; c) dans chaque éprouvette on a versé 40 ml solution éthanol-eau d'une certaine fraction molaire (x_2); d) on a recouvert les éprouvettes et on les a fait agiter pendant 3...4 heures après quoi leur contenu a été filtré quantitativement par des creusets à filtrer dont la tare a été déterminée antérieurement. De cette manière on a retenu la résine imbibée d'éthanol et eau.

Pour éliminer les deux solvants absorbés à la surface de la résine les creusets sont introduits dans des éprouvettes spéciales, métalliques, qu'on les soumet à une centrifugation durant 20 min. à une vitesse de 16 000 rot/min. Pour déterminer la quantité d'eau absorbée par une quantité donnée de résine (après centrifugation) on a fait appel à la méthode Karl Fischer:



On établit la quantité d'éthanol (ainsi que la fraction molaire $\bar{x}_s$) ayant en vue la différence entre la quantité de résine à analyser et la quantité d'eau qu'elle contient, après la solvation de l'échangeur d'ions obtenue avec des molécules de ce solvant.

3. Résultats et discussion

Selon ce qu'on connaît [1], l'effet du milieu peut être apprécié par $\log_m \gamma$, une constante physique se rapportant à la différence entre les énergies libres standard qui correspondent à une substance dissoute en eau et un solvant non aqueux à concentration réduite.

Tout d'abord on a étudié la solvation sélective de la résine échangeuse d'ions de type Dowex 50WX8 sous la forme : RH, RK et R_2UO_2 en divers mélanges d'éthanol-eau. On en présente les résultats dans les tableaux 1...3 et la fig. 1. Dans cette figure on a représenté l'interdépendance entre la fraction molaire de l'éthanol dans le mélange initial éthanol-eau (x_s) et la fraction molaire du même solvant organique après la solvation de la résine donnée ($\bar{x}_s$).

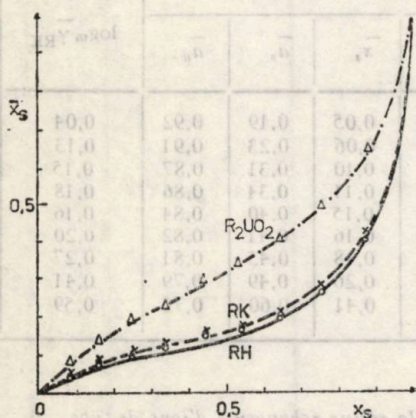


Fig. 1. — L'interdépendance entre les fractions molaires du solvant organique avant (x_s) et après la solvation ($\bar{x}_s$) des résines RH, RK et R_2UO_2 .

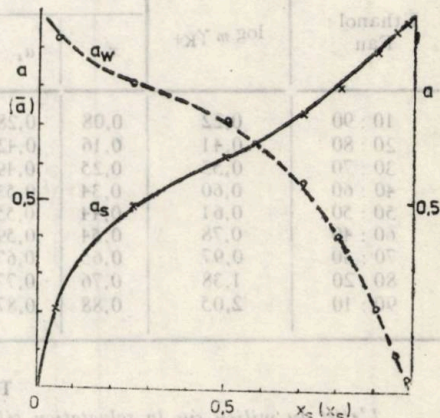


Fig. 2. — La dépendance des activités dans l'eau (a_w) et dans le mélange eau-éthanol (a_s) de la fraction molaire du solvant organique.

Pour calculer l'effet du milieu sur la solvation sélective des résines RH, RK et R_2UO_2 (v. les tableaux 1...3) on a employé la formule :

$$(1) \quad \log_m \bar{\gamma}_{RA} = n x_s \left(\log \frac{\bar{a}_w}{\bar{a}_s} - \log \frac{a_w}{a_s} \right),$$

RA représentant le symbole pour la résine choisie : RH, RK et R_2UO_2 . Dans cette relation x_s représente la fraction molaire du solvant organique avant la solvation et $\bar{a}_w$, $\bar{a}_s$, a_w et a_s se rapportent aux activités de l'es-

Tableau 1

L'effet du milieu sur la solvation sélective de la résine échangeuse d'ions de type Dowex 50WX8 sous la forme RH

Éthanol : Eau	$\log m \gamma_{H^+}$							$\log m \bar{\gamma}_{RH}$
		x_s	a_s	a_w	$\bar{x}_s$	$\bar{a}_s$	$\bar{a}_w$	
10 : 90	0,08	0,08	0,28	0,90	0,04	0,15	0,93	0,09
20 : 80	0,06	0,16	0,42	0,84	0,06	0,22	0,92	0,21
30 : 70	-0,06	0,25	0,49	0,81	0,09	0,28	0,89	0,32
40 : 60	-0,32	0,34	0,53	0,79	0,10	0,30	0,88	0,36
50 : 50	-0,62	0,44	0,55	0,77	0,11	0,33	0,87	0,37
60 : 40	-0,80	0,54	0,59	0,75	0,14	0,39	0,86	0,40
70 : 30	-0,86	0,65	0,67	0,67	0,17	0,43	0,84	0,52
80 : 20	-0,67	0,76	0,77	0,49	0,23	0,48	0,81	0,79
90 : 10	-0,46	0,88	0,87	0,26	0,36	0,58	0,79	1,24

Tableau 2

L'effet du milieu sur la solvation sélective de la résine échangeuse d'ions de type Dowex 50WX8 sous la forme RK

Éthanol : Eau	$\log m \gamma_{K^+}$							$\log m \bar{\gamma}_{RK}$
		x_s	a_s	a_w	$\bar{x}_s$	$\bar{a}_s$	$\bar{a}_w$	
10 : 90	0,22	0,08	0,28	0,90	0,05	0,19	0,92	0,04
20 : 80	0,41	0,16	0,42	0,84	0,06	0,23	0,91	0,13
30 : 70	0,55	0,25	0,49	0,81	0,10	0,31	0,87	0,15
40 : 60	0,60	0,34	0,53	0,79	0,11	0,34	0,86	0,18
50 : 50	0,61	0,44	0,55	0,77	0,15	0,40	0,84	0,16
60 : 40	0,78	0,54	0,59	0,75	0,16	0,41	0,82	0,20
70 : 30	0,97	0,65	0,67	0,67	0,18	0,45	0,81	0,27
80 : 20	1,38	0,76	0,77	0,49	0,26	0,49	0,79	0,41
90 : 10	2,05	0,88	0,87	0,26	0,41	0,60	0,75	0,59

Tableau 3

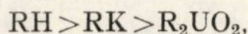
L'effet du milieu sur la solvation sélective de la résine échangeuse d'ions de type Dowex 50WX8 sous la forme R_2UO_2

Éthanol : Eau	$\log m \gamma_{U(VI)}$							$\log m \bar{\gamma}_{R_2UO_2}$
		x_s	a_s	a_w	$\bar{x}_s$	$\bar{a}_s$	$\bar{a}_w$	
10 : 90	-0,64	0,08	0,28	0,90	0,08	0,28	0,90	0,006
20 : 80	-1,05	0,16	0,42	0,84	0,13	0,36	0,86	0,017
30 : 70	-0,77	0,25	0,49	0,81	0,17	0,43	0,84	0,021
40 : 60	-0,19	0,34	0,53	0,79	0,21	0,47	0,82	0,023
50 : 50	0,47	0,44	0,55	0,77	0,27	0,50	0,80	0,024
60 : 40	1,34	0,54	0,59	0,75	0,32	0,52	0,79	0,033
70 : 30	2,32	0,65	0,67	0,67	0,38	0,54	0,78	0,061
80 : 20	3,50	0,76	0,77	0,49	0,48	0,56	0,76	0,118
90 : 10	4,04	0,88	0,87	0,26	0,64	0,67	0,68	0,108

pèce de dilution infinie dans l'eau (w) et dans le mélange de solvants (s) après et avant la solvation. Les valeurs de ces activités (pour une valeur donnée de x_s , respectif $\bar{x}_s$) sont prélevées de la fig. 2. On a conçu cette représentation graphique en usant des données obtenues par Shaw et Butler [17] se rapportant au comportement des électrolytes dans des mélanges de solvants (pour le cas où la concentration de LiCl est nulle).

Dans la relation (1) n représente le nombre de molécules de solvant organique se situant à la proximité du cation de la résine de type RH, RK et R_2UO_2 pour une fraction molaire initiale quelconque. Ce nombre est calculé en utilisant la représentation graphique de la fig. 3 qui précise l'interdépendance entre la fraction molaire (x_s) et le nombre de moles de solvant organique qui ont été absorbés par une quantité de 1 g de résine sèche.

En ce qui concerne la disposition des molécules d'eau et de solvant organique dans une résine échangeuse d'ions, à cause d'un nombre plus grand de degrés de liberté de rotation de l'anion, une attraction plus prononcée se produit pour les molécules d'eau que pour celles de solvant organique [7]. Par conséquent ces dernières vont s'approcher du cation en provoquant la solvation. En ce cas le nombre de molécules de solvant organique qui solvate le cation de la résine donnée, pour une valeur de x_s , diminue selon l'ordre suivant :



Il en résulte d'ici que la solvation est plus prononcée pour les ions ayant les rayons ioniques plus petites que pour ceux plus volumineux, ce qui s'explique par l'effet polarisant plus prononcé sur les molécules de solvant respectives exercé par les ions plus petits par rapport à celui des ions plus grands.

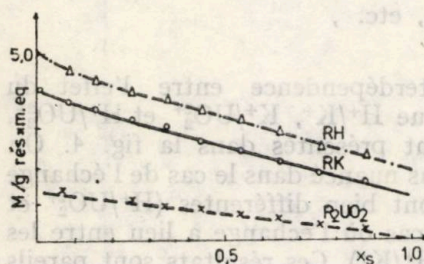


Fig. 3. — La variation du nombre de moles de solvant organique absorbés dans la résine (g.m. équivalent) fonction de la fraction molaire de l'éthanol.

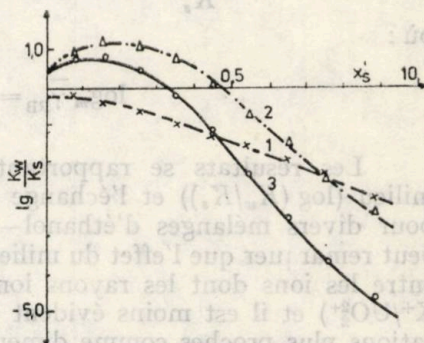
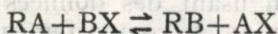


Fig. 4. — L'effet du milieu sur l'échange ionique H^+/K^+ (1), K^+/UO_2^{2+} (2) et H^+/UO_2^{2+} (3), pour divers mélanges d'éthanol—eau.

Les valeurs se rapportant à la solvation sélective des ions singuliers H^+ et K^+ (c'est-à-dire $\log_m \gamma_{H^+}$ et $\log_m \gamma_{K^+}$) ont été fournies par [3]; les valeurs qui correspondent à $\log_m \gamma_{U(VI)}$, caractéristiques pour la solvation de l'ion d'uranyle se trouvant dans une combinaison anorganique simple, sont celles indiquées dans [5].

L'effet du milieu pour le cas de l'échange cationique: H^+/K^+ , K^+/UO_2^{2+} et H^+/UO_2^{2+} peut être réduit de la sorte [18]:

Pour la réaction générale d'échange ionique:



la constante d'équilibre sera:

$$(2) \quad K = \frac{[RB][AX]}{[RA][BX]}$$

Si l'on remplace les concentrations avec les activités et si l'on a en vue la réalisation de cet échange ionique en eau (w) et en mélange éthanol-eau (s), à une température donnée, la relation de la constante d'équilibre pour les deux cas sera:

$$(2') \quad K_w = \frac{\bar{a}_{RB}^w \bar{a}_{AX}^w}{\bar{a}_{RA}^w \bar{a}_{BX}^w}, \quad (2'') \quad K_s = \frac{\bar{a}_{RB}^s \bar{a}_{AX}^s}{\bar{a}_{RA}^s \bar{a}_{BX}^s}$$

Ensuite on effectue le rapport des deux expressions et on passe au logarithme, d'où il en résulte:

$$(3) \quad \log \frac{K_w}{K_s} = \log_m \bar{\gamma}_{RB} - \log_m \bar{\gamma}_{RA} + \log_m \gamma_{AX} - \log_m \gamma_{BX}$$

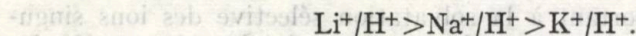
ou:

$$(3') \quad \log \frac{K_w}{K_s} = \log_m \bar{\gamma}_{RB} - \log_m \bar{\gamma}_{RA} + \log_m \gamma_A - \log_m \gamma_B,$$

où:

$$\log_m \bar{\gamma}_{RB} = \log \frac{\bar{a}_{RB}^w}{\bar{a}_{RB}^s}, \text{ etc. ,}$$

Les résultats se rapportant à l'interdépendance entre l'effet du milieu ($\log(K_w/K_s)$) et l'échange cationique H^+/K^+ , K^+/UO_2^{2+} et H^+/UO_2^{2+} , pour divers mélanges d'éthanol-eau, sont présentés dans la fig. 4. On peut remarquer que l'effet du milieu est plus nuancé dans le cas de l'échange entre les ions dont les rayons ioniques sont bien différentes (H^+/UO_2^{2+} et K^+/UO_2^{2+}) et il est moins évident pour le cas où l'échange a lieu entre les cations plus proches comme dimensions (H^+/K^+). Ces résultats sont pareils à ceux que Gupta [18]...[20] a trouvé lors de l'étude de la sélectivité de l'échangeur d'ions de type PSS en mélanges de solvants. De la sorte, le logarithme de la constante d'équilibre pour un mélange eau-méthanol augmente suivant l'ordre ci-dessous de l'interchangement:



Cette observation s'explique par le fait que l'énergie libre standard caractéristique à l'échange cationique est différente suivant la dimension (et la charge) des ions qui changent. L'échange de deux ions à rayon ionique

différente est effectué sur le compte d'une variation augmentée de l'énergie libre standard (donc, un effet du milieu plus évident que pour le cas où cet échange aurait lieu entre deux ions dont les dimensions sont plus proches).

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SOLVATAREA SELECTIVĂ A UNOR RĂȘINI SCHIMBĂTOARE DE IONI DE TIPUL DOWEX 50WX8, ÎN AMESTECURI DE ETANOL-APĂ

(Rezumat)

Se studiază procesul de solvatare selectivă a unor rășini schimbătoare de ioni de tipul Dowex 50WX8 încărcate cu ioni de H^+ , K^+ și UO_2^{2+} , în diferite amestecuri de etanol-apă. S-a estimat efectul mediului ($\log m_{YRA}^-$) asupra solvătării preferențiale a cationilor H^+ , K^+ și UO_2^{2+} din rășinile date, stabilindu-se numărul de molecule de solvent organic care au solvatat ionii respectivi. Acest număr descrește în ordinea: $RH > RK > R_2UO_2$, datorită polarizării diferite a moleculelor de solvent organic de către cationii respectivi. În final s-a investigat efectul mediului ($\log (K_w/K_s)$) asupra schimbului cationic H^+/K^+ , K^+/UO_2^{2+} și H^+/UO_2^{2+} din rășinile de tipul Dowex 50WX8, în diferite amestecuri de etanol-apă.

différente est effectuée sur le compte d'une variation augmentée de l'énergie libre standard (donc, un effet du milieu plus évident que pour le cas où cet échange aurait lieu entre deux ions dont les dimensions sont plus proches).

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SOLVATAREA SELECTIVĂ A UNOR RAȘINI SCHIMBĂTOARE DE IONI DE TIPUL DOWEX 50WXS ÎN AMESTECURI DE ETANOL-APĂ

(Rezumat)

Se studiază procesul de solvatare selectivă a unor rășini schimbătoare de ioni de tipul Dowex 50WXS încărcate cu ioni de H^+ , K^+ și UO_2^{2+} , în diferite amestecuri de etanol-apă. S-a estimat efectul mediului (ion H^+) asupra solvabilității preferențiale a cationilor H^+ , K^+ și UO_2^{2+} din rășinile date, stabilindu-se numărul de molecule de solvent organic care în solvatarea ionii respective. Acest număr descree în ordine: $RH > RK > RUO_2$, datorită polarității diferite a moleculelor de solvent organic de către cationii respective. În final s-a investigat efectul mediului (ion K^+) asupra schimbării cationicilor H^+ , K^+ și UO_2^{2+} din rășinile de tipul Dowex 50WXS, în diferite amestecuri de etanol-apă.

DÉTERMINATION SPECTROPHOTOMÉTRIQUE DU THALLIUM (III) AVEC LA *p*-PHÉNYLÉNEDIAMINE

PAR

M. FURNICĂ

1. Introduction

La littérature de spécialité rassemble un grand nombre de travaux dans lesquels on utilise la *p*-phénylènediamine (*p*-Ph.DA) à la détermination spectrophotométrique de quelques substances à caractère oxydant, par exemple, V(V) [1], Au(III) [2], Os(VIII) [3], Fe(III) [4], etc., en se basant sur la coloration qui résulte par l'oxydation de celle-ci [5].

Dans le présent travail on utilise la possibilité de déterminer par voie spectrophotométrique le Tl(III) par la PhDA, profitant du fait que le système Tl(III)/Tl(I) possède un potentiel élevé ($E_0 = 1,25$ V [6]) et du fait que la *p*-PhDA est un réducteur puissant.

2. Partie expérimentale

2.1. Réactifs

On a préparé la solution initiale de Tl(III), en oxydant le Tl_2SO_4 avec l'eau de brome, en dissolvant 0,6176 g Tl_2SO_4 (ANALAR) dans un volume approchant de 25 ml d'eau distillée, en ajoutant 0,5 ml H_2SO_4 concentré ; on ajoute de l'eau de brome jusqu'à ce que la solution vire au jaune. On élimine l'excès de brome en passant un courant d'air pendant une demi-heure, jusqu'à la décoloration. On passe la solution en lavant avec de l'eau distillée, dans un ballon jaugé de 100 ml. Pour effectuer les expériences on prend chaque fois 10 ml de la solution initiale de Tl(III) en la diluant jusqu'à 50 ml. La solution ainsi obtenue a la concentration de 1 mg Tl/ml et le pH=1,5.

On prépare la solution de *p*-PhDA en dissolvant une quantité déterminée de *p*-PhDA purifiée par sublimation, dans de l'eau distillée. Pour les expériences on a utilisé chaque fois une solution fraîche de PhDA, ayant une concentration de 0,1 mg/100 ml.

2.2. Appareillage

Les déterminations de l'absorbance ont été effectuées à l'aide d'un spectrophotomètre de type SPECOL à cuve de 1 cm. On a mesuré le pH des

solutions avec un électrode en verre, en utilisant un pH-mètre MV-85 et les variations du pH ont été réalisées à l'aide des solutions tampon selon Sørensen et Walpole.

2.3. Le spectre d'absorption

Le spectre d'absorption des solutions colorées obtenues après la réaction du Tl(III) avec la *p*-PhDA à un pH=6 et dans un excès de *p*-PhDA est représenté dans la Fig. 1. On observe que l'absorbance maxima se situe entre 460 et 500 nm.

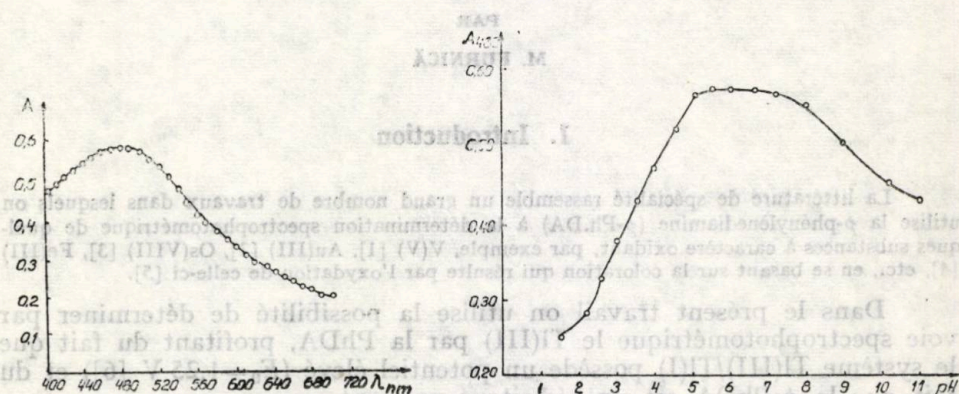


Fig. 1. — Spectre d'absorption des solutions de Tl(III) avec la *p*-PhDA.

Fig. 2. — Variations de l'absorbance des solutions de Tl(III) avec la *p*-PhDA, en fonction du pH

Pour établir l'influence des différents paramètres sur l'intensité de la coloration, les mesures de l'absorbance ont été effectuées à 480 nm.

2.4. L'influence du pH

En étudiant l'absorbance des solutions colorées de Tl(III) avec la *p*-PhDA, en fonction du pH, on a constaté que la valeur maxima se situe entre 5 et 7 unités de pH (Fig. 2). Par conséquent on a effectué les déterminations à un pH=6.

2.5. L'influence de la quantité de réactif

En ajoutant des quantités différentes de *p*-PhDA à la même quantité de Tl(III), on constate que même une quantité de dix fois plus grande que celle nécessaire, n'influence en rien l'absorbance mesurée à 480 nm. La variation de l'absorbance en fonction de la quantité de réactif est représentée dans la Fig. 3. Dans les expériences ultérieures on a utilisé un ml de solution de *p*-PhDA pour chaque échantillon de Tl(III).

2.6. La stabilisation dans le temps de la coloration des solutions de $Tl(III)$ avec la p -PhDA

En effectuant la réaction entre le $Tl(III)$ et la p -PhDA dans les conditions établies de pH et de la quantité de réactif, on a constaté que la coloration arrive immédiatement à la valeur maxima qui se maintient constante plus d'une demi heure; le temps suffit pour la préparation des échantillons suivants et l'effectuation des mesures. La variation de l'intensité de la coloration fonction de temps est illustrée par les données du tableau 1.

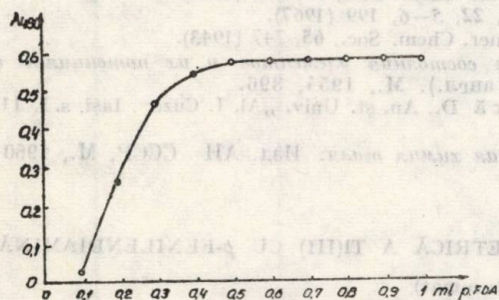
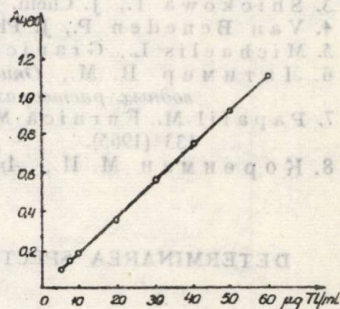
Tableau 1

Les valeurs de l'absorbance en fonction de temps pour une solution de 0,3 mg $Tl(III)$ et 1 mg p -PhDA

Temps, [min.]	3	5	10	15	20	25	30
Absorbance à 480 nm	0,57	0,57	0,57	0,57	0,57	0,57	0,57

2.7. Vérification de la loi Bouguer-Lambert-Beer

Pour vérifier la loi Bouguer-Lambert-Beer, dans les conditions de travail établies, on a pris des volumes différents de la solution de $Tl(III)$ à une concentration de 1 mg/ml et on a ajouté 1 ml de la solution de p -PhDA et 7 ml d'une solution tampon d'acétate - acide acétique, à pH=6, en la complétant avec de l'eau distillée jusqu'au volume de 10 ml.

Fig. 3.— Variation de l'absorbance en fonction de la quantité de p -PhDA.Fig. 4.— Variation de l'absorbance des solutions de $Tl(III)$ avec la p -PhDA, en fonction de la concentration en $Tl(III)$

L'absorbance de chaque échantillon a été déterminée à 480 nm. Les résultats obtenus sont présentés dans la Fig. 4. Il en résulte que la loi de Bouguer-Lambert-Beer est respectée dans le domaine de concentration située entre 5 et 60 μg $Tl(III)/ml$.

La valeur élevée du coefficient molaire d'extinction (38 000) situe la méthode parmi les méthodes sensibles de détermination spectrophotométrique du Tl(III) [8].

2.8 Influences des ions étrangers

Ayant en vue la possibilité d'appliquer la méthode dans la pratique analytique on a effectué des recherches concernant l'effet de la présence de différents ions à caractère oxydant à côté du Tl(III), sur l'intensité de la coloration. Des données obtenues dans les différentes expériences on a constaté que les ions et en général les substances oxydantes empêchent la détermination du Tl(III) avec la *p*-PhDA, parce qu'ils produisent la même coloration.

3. Conclusions

On a établi les conditions dans lesquelles la réaction de couleur entre le Tl(III) et la *p*-PhDA peut être utilisée à la détermination spectrophotométrique du Tl(III). L'absorbance maxima a lieu à 480 nm. La loi de Bouguer-Lambert-Beer est respectée dans le domaine de concentration de 5 à 60 $\mu\text{g/ml}$.

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Institut Polytechnique, Jassy,
Chaire de Chimie Physique

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DETERMINAREA SPECTROFOTOMETRICĂ A Tl(III) CU *p*-FENILENDIAMINĂ

(Rezumat)

Se propune o metodă de dozare spectrofotometrică a Tl(III) bazată pe reacția de culoare pe care acești ioni o dau cu *p*-fenilendiamina la $\text{pH}=6$. Absorbția maximă are loc la o lungime de undă de 480 nm. Legea lui Bouguer-Lambert-Beer este respectată în domeniul de concentrație cuprins între 5 și 60 $\mu\text{g Tl/ml}$.

EXPLOITATION OF THE WASTE MOLECULAR SIEVES

BY

M. CRUCEANU and EVELINA POPOVICI

1. Introduction

During the last two decades, the petrochemical industry has obtained remarkable technological progresses by utilization, at large scale, of the zeolite molecular sieves, due to their both high efficient selective adsorption capacity and catalytic properties. The continuous increase of these products demand, to be used in both classical and new processes, has determined a rapid development of their production. But, at the same time, as a direct consequence, the important quantities of waste molecular sieves are annually removed without a precise destiny. In the case of the molecular sieves employed as catalyst, containing metals, up to now investigations has in view, the recovery of components having catalytic activity without paying attention to their zeolite support.

In a previous paper [1] there was reported the results as regards the behaviour of molecular sieves to action of mineral acids, finding the fact that the depth of acid degradation is dependent directly on nature and concentration of the acid, temperature, time as well as on their type. On the basis of these results, the present paper deals with solubility of certain molecular sieves in acid medium as well as the possibility of their regeneration through precipitation and hydrothermal crystallization in order to obtain some zeolite adsorbents.

2. Experimental

The experiments were performed using waste molecular sieves such as SMP-4, SMP-5 and USIMO, removed from drying columns employed for gases in an oil field for eight months.

The waste molecular sieves were solubilized in dilute hydrochloric acid solutions, obtaining after filtration, an acid extract (Table 1).

Based on their chemical analysis (Table 2), the acid extracts were neutralized, under stirring, with either sodium hydroxide or organic bases. In order to realize the strong alkaline medium, demanded by hydrothermal synthesis, there was added a controlled amount of sodium hydroxide to the extracts.

The structural adsorptive properties of the obtained products were compared with those of the original molecular sieves.

Table 1

Operating Conditions

Product	Acid treatment				Neutralized with	Overall yield %	Remarks
	Temp. °C	HCl %	solid/liquid ratio	acid extract concentration g/100 g solvent			
1 a	70	3.6	1:25	3.1	NaOH	92.3	SMP-4 original
1 b	90	3.6	1:25	3.3	NaOH	95.0	
2 a	70	3.6	1:25	2.6	NaOH	68.4	SMP-5 regenerated
2 b	90	3.6	1:25	2.8	NaOH	72.5	
3 a	70	3.6	1:25	1.8	NaOH	50.2	SMP-4 waste
3 b	90	3.6	1:25	2.1	NaOH	57.5	
4 a	70	3.6	1:25	1.8	Pyridina	49.2	SMP-4 waste
4 b	90	3.6	1:25	2.1	Pyridina	52.5	
5 a	70	3.6	1:25	2.3	NaOH	61.3	DUSIMO waste
5 b	90	3.6	1:25	2.5	NaOH	64.1	

Table 2

Chemical Composition of Extracts

Product	Acid extract		Neutralized extract	
	Na ₂ O/Al ₂ O ₃	SiO ₂ /Al ₂ O ₃	Na ₂ O/Al ₂ O ₃	SiO ₂ /Al ₂ O ₃
1 b	0.69	1.85	2.29	1.85
2 b	1.01	2.06	4.19	2.06
3 b	0.42	1.33	3.42	1.33
5 b	0.33	1.36	2.28	1.36

Determination of the solubility, chemical analyses and adsorptive properties were carried out according to usual laboratory technique [2], [3], [8], [10].

The data, as regards the overall yield of the solubilization — precipitation + crystallization process, are summarized in Table 1, too.

3. Results and Discussion

The investigated molecular sieves are soluble in 1 n hydrochloric acid solution, in proportion ranging from 45 to 80%, depending on temperature and their degradation degree caused by their long exploitation. By filtration, there were separated acid extracts which have concentrations ran-

ging between 1.8 and 3.3 g solid substance dissolved in 100 g solvent. Their chemical analysis had pointed out values of molar ratios, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$, ranging from 0.33 to 1.01 and 1.33 to 2.06 respectively.

Neutralization of the acid extract was realized using dilute solutions of sodium hydroxide or organic bases in such a manner that the chemical composition of the reactant mixture to be placed in the field of initial concentrations (Fig. 1), which generate molecular sieves by NaA type [4].

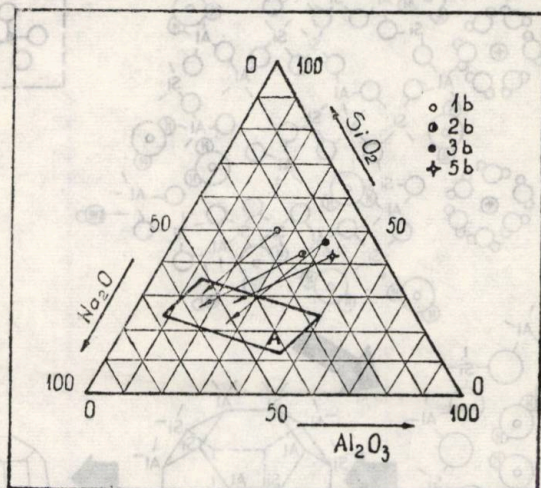


Fig. 1. — Field of the initial chemical composition.
A — Field that generate NaA molecular sieves;
o — 1b, o — 2b, ● — 3b, + — 5b — composition of the acid extract.

The gelatinous product obtained was submitted to crystallization according to usual technique of the molecular sieves hydrothermal synthesis. Within 7...15 hours, there was obtained a solid products, in white colour. The overall yield of the solubilization—precipitation—crystallization process was ranged from 50 to 90%.

Elaboration of the process as regard the exploitation of waste molecular sieves was based on intimate mechanism of the molecular sieves formation and crystallization.

According to Barrer's concept [2] that the crystalline edifice of molecular sieves is a polycondensation polymer, realized by packing of some units, then called by Kerr [5] the soluble species, we consider the solubilization process as being a dismemberment process of the crystalline elemental cell in its component parts, represented by soluble species, made up by chains of silicon and aluminium tetrahedrons and polyhedrons.

Accepting the existence of soluble species in the acid extract, it is to be expected that their sizes, ratio between species as well as the order silicon and aluminium tetrahedrons chain formation to depend on temperature, acid concentration and residence time, facts proved experimentally. Separation and identification of these soluble species was already reported [6], [7].

Based on the mechanism formulated by Kerr as regard the formation of cubeoctahedrons by soluble species rearrangement around the hydrated sodium ions (Fig. 2), we considered that by controlling neutralization of the acid extract, it is possible to be started the nucleation needed for the formation of a new zeolite structure.

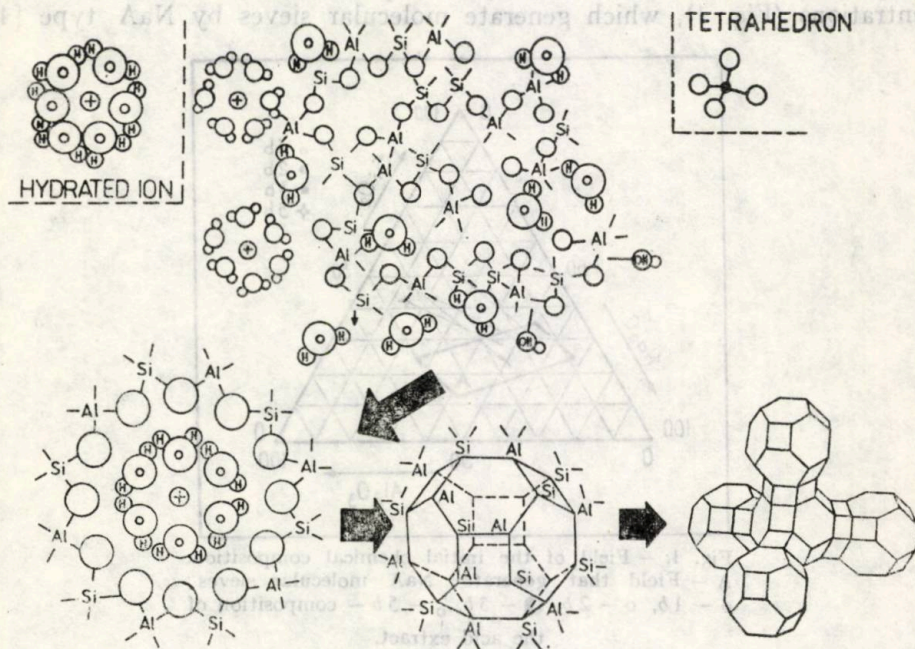


Fig. 2.— Illustration of the mechanism of crystalline structure formation [5].

The obtained products were tested from the view point of statical adsorption capacity against water and benzene vapour. There are compared the values of adsorption capacity of the original molecular sieves, waste molecular sieves and those obtained by acid solubilization and alkaline precipitation (Table 3).

Table 3
Statical Adsorbption Capacity (24°C)

Product	Adsorbption water			Adsorption benzene		
	Original	Waste	After processing	Original	Waste	After processing
1 b	22.14	20.10	26.5	3.66	14.1	4.11
2 b	22.14	14.91	18.5	3.66	8.9	7.43
3 b	22.14	9.86	17.6	3.66	9.3	5.20
4 b	22.14	17.90	19.3	3.66	8.7	7.41
5 b	24.3	14.60	19.3	3.47	12.0	4.63

In the X-ray diffraction spectrum of the obtained products there are identified many lines proper to molecular sieves by NaA type.

It must be remarked the fact that the exploitation of the waste molecular sieves is possible by the suggested process [10] because the crystalline adsorbents with high adsorption capacity against polar small molecules, as well as a good selectivity against benzene, proper for molecular sieves.

Based on these experimental data, the technological flux for waste molecular sieves exploitation, as given below, was established (Fig. 3).

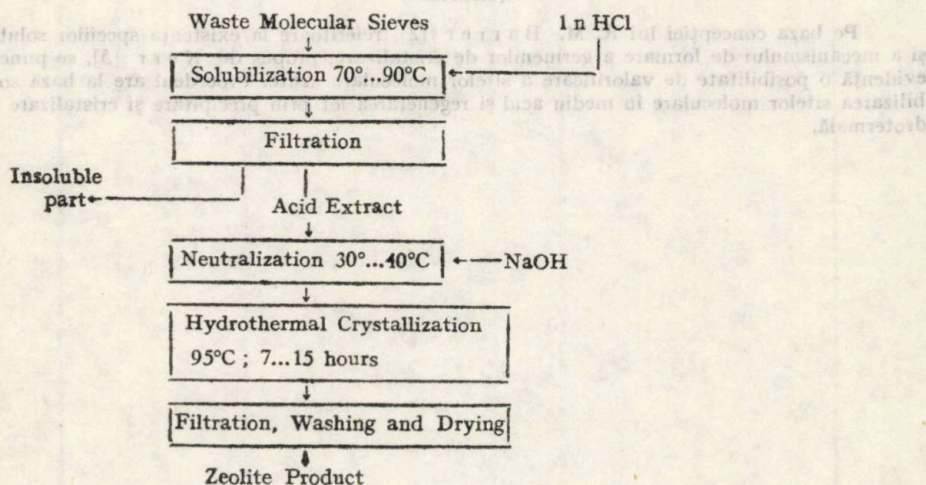


Fig. 3.— Flow diagram of the process for waste molecular sieves exploitation.

The elaborated process allows equally the exploitation of the molecular sieves resulted from noncorresponding charges, wastes resulted from granulation as well as the molecular sieves from drying and adsorption columns, with low adsorption capacity or mechanically degraded causing the increase of pressure drop on the columns.

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VALORIFICAREA SITELOR MOLECULARE UZATE

(Rezumat)

Pe baza concepției lui R. M. Barrer [2], referitoare la existența speciilor solubile și a mecanismului de formare a germinilor de cristalizare, propus de Kerr [5], se pune în evidență o posibilitate de valorificare a sitelor moleculare uzate. Procedul are la bază solubilizarea sitelor moleculare în mediu acid și regenerarea lor prin precipitare și cristalizare hidrotermală.

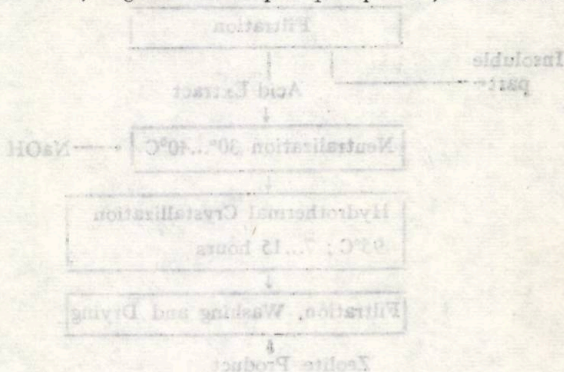


Fig. 1—Flow diagram of the process for waste molecular sieves exploitation.

The elaborated process allows equally the exploitation of the molecular sieves resulted from noncorresponding charges, wastes resulted from granulation as well as the molecular sieves from drying and adsorption columns, with low adsorption capacity or mechanically debilitated causing the increase of pressure drop on the columns.

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STUDIUL PROPRIETĂȚILOR ACIDE ALE ZEOLIȚILOR CONȚINÎND PĂMÎNTURI RARE

DE

EVELINA POPOVICI, N. NAUM, GH. MIHĂILĂ ȘI V. ABABI

1. Introducere

Proprietățile catalitice ale zeoliților, cercetate în diverse lucrări [1]...[5], au scos în evidență necesitatea aprofundării studiului influenței factorilor chimico-structurali asupra naturii acide a suprafeței catalizatorilor.

Principalii factori structurali care influențează caracterul acid al suprafeței catalizatorilor sînt: raportul molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ [6] și gradul de dehidroxilare [7]. Acești factori cooperează cu cei de natură chimică, dintre care cei mai importanți sînt: natura cationilor de schimb [8] și gradul de decationizare [9].

Influența cumulată a acestor factori explică aspectele complexe care caracterizează formele de existență a acidității pe suprafața catalizatorilor zeolitici.

Studiile cele mai recente au confirmat existența centrilor acizi de tărie diferită. Tăria acestor centri poate fi însă mult influențată de acțiunea polarizantă a cationilor vecini, care tind să elibereze un proton din legătura lor hidroxilică, ceea ce are drept efect mărirea acidității hidrogenului din gruparea hidroxil. Această influență inductivă poate fi exercitată în mod egal și de către defectele structurale ale rețelei [10], prin intermediul cîmpului cristalin.

Studiile privind variația constantei dielectrice a sistemelor zeolitice supuse excitării în curent alternativ, în domenii largi de frecvență și de temperatură, au permis introducerea unui nou concept, de centru activ dinamic, specific numai structurilor zeolitice. Acesta poate fi cîmp electric dinamic, centru acid Lewis dinamic sau centru acid Brönsted dinamic [11].

În cele ce urmează se analizează proprietățile acide ale unor catalizatori utilizați în reacția de alchilare a toluenului cu seria de alcooli $\text{C}_1 \dots \text{C}_3$.

2. Partea experimentală

Produsele zeolitice cercetate provin de la firmele Linde și Norton și au fost supuse schimbului ionic cu soluție 0,1 M azotat de ceriu, respectiv azotat de lantan, timp de 2 ore, la temperatura de 85°C. Operația de schimb ionic s-a repetat de șase ori, fiecare operație fiind urmată de filtrare, spălare și uscare la 110°C. În final produsele au fost calcinate treptat la 500°C, timp de 12 ore. Compoziția chimică a produselor deshidratate s-a determinat prin fluorescență cu un aparat de raze X, tip Philips Norelco 300.

Determinarea acidității totale și a celei protonice s-a efectuat pe baza reacției de schimb a ionilor metalelor alcaline cu centrul acizi ai catalizatorului, în absența, respectiv prezența fluorurii de sodiu în exces [12].

Evaluarea distribuției acidității s-a efectuat prin metoda titrării cu *n*-butilamină în mediu de benzen anhidru în prezența unor indicatori H a m e t t și aril-metanolici [13].

În paralel s-a efectuat și determinarea suprafeței specifice printr-o metodă gravimetrică a adsorbției dinamice a vaporilor de benzen din curent de gaz purtător, folosind o balanță cu fir de cuarț [14].

3. Rezultate și discuții

Rezultatele experimentale ale analizei chimico-structurale sînt prezentate în tabelul 1, iar cele referitoare la aciditatea produselor sînt indicate în tabelul 2.

Tabelul 1

Analiza chimico-structurală a catalizatorilor

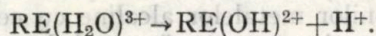
Produsul	Structură zeolitică	Cation de schimb	Grad de schimb %	Raport molar $\text{SiO}_2/\text{Al}_2\text{O}_3$	Suprafață specifică m^2/g
N_1	X	Ce	89,90	2,48	814,25
N_2	X	Ce	87,10	3,10	712,08
N_3	Y	Ce	83,78	5,36	770,12
N_4	Mordenit	Ce	34,83	10,00	438,14
N_5	X	La	84,01	2,48	822,08
N_6	X	La	85,00	3,10	708,52
N_7	Y	La	90,14	5,36	782,01
N_8	Mordenit	La	33,88	10,00	445,08

Determinarea acidității drept criteriu al activității constituie o problemă complexă deoarece nu este suficient să se cunoască numai tăria centrilor acizi pe suprafața catalizatorului ci și natura acestor centri.

Metoda experimentală utilizată în studiul acidității permite evaluarea distinctă a acidității protonice și a acidității totale, respectiv evaluarea contribuției acidității neprotonice. Rezultatele din tabelul 2 scot în evidență faptul că prezența ionilor de Ce^{3+} și La^{3+} , în structurile zeolitice, contribuie la dezvoltarea unei acidități totale, care poate asigura o activitate catalitică deosebită. De asemenea se observă că aciditatea neprotonică a catalizatorilor studiați scade odată cu creșterea raportului molar $\text{SiO}_2/\text{Al}_2\text{O}_3$, în timp ce aciditatea protonică depinde de natura cationului, de gradul de schimb precum și de raportul molar $\text{SiO}_2/\text{Al}_2\text{O}_3$.

Se cunoaște faptul că sursa acidității protonice în sistemele zeolitice o constituie prezența grupărilor OH acide, care asigură activitatea catalitică de tip ion de carboniu.

Numărul grupărilor OH acide poate fi calculat și ținînd cont de conținutul de ceriu, respectiv lantan, prezent în zeolit, pe baza unei relații date [15] ce se sprijină pe ideea că fiecare ion de RE^{3+} furnizează un loc acid Brönsted:



Tabelul 2

Valori ale acidității produselor cercetate

Produsul	Aciditate totală mechiv/g	Aciditatea protonică		Aciditatea neprotonică		Aciditatea protonică calculată g O-H ⁺ /m ²
		mechiv/g	echiv/m ²	mechiv/g	echiv/m ²	
N ₁	5,85	4,83	3,44 · 10 ¹⁸	1,02	0,75 · 10 ¹⁸	3,9 · 10 ¹⁸
N ₂	5,73	4,98	4,08 · 10 ¹⁸	0,83	0,69 · 10 ¹⁸	4,4 · 10 ¹⁸
N ₃	5,76	5,12	4,14 · 10 ¹⁸	0,64	0,49 · 10 ¹⁸	4,2 · 10 ¹⁸
N ₄	2,97	2,83	3,84 · 10 ¹⁸	0,14	0,19 · 10 ¹⁸	3,7 · 10 ¹⁸
N ₅	5,88	4,70	3,42 · 10 ¹⁸	1,18	0,84 · 10 ¹⁸	3,7 · 10 ¹⁸
N ₆	4,06	3,14	2,64 · 10 ¹⁸	0,92	0,78 · 10 ¹⁸	4,4 · 10 ¹⁸
N ₇	4,89	4,26	3,24 · 10 ¹⁸	0,63	0,48 · 10 ¹⁸	4,1 · 10 ¹⁸
N ₈	2,39	2,16	2,88 · 10 ¹⁸	0,23	0,30 · 10 ¹⁸	2,8 · 10 ¹⁸

Această observație, demonstrată experimental [15], [16], a permis calcularea numărului de locuri OH acide și densitatea acestora pe suprafața catalizatorilor (tabelul 2).

Rezultatele sînt în concordanță cu cele obținute experimental și subliniază faptul că pe suprafața catalizatorilor cercetați predomină o distribuție densă a centrilor acizi Brönsted, care depinde de conținutul de ioni de ceriu sau lantan.

Se știe că aciditatea îmbracă pe suprafața zeoliților țării acide diferite, pentru a căror evidențiere s-a folosit metoda N. A. Benesi, care se bazează pe neutralizarea succesivă a locurilor acide cu *n*-butilamină, în suspensii neapoase, în prezența unor indicatori Hammett și arilmetanolitici.

În general, centrii cu o aciditate $H_0 < -8,2$ au fost numiți centri acizi puternici; cei cu $-8,2 < H_0 < -3,0$, centri acizi intermediari și cei cu $-3,0 < H_0 < +3,3$, centri acizi slabi, iar centrii acizi cu $H_R = -13,3$, centri acizi foarte puternici.

Spectrul de aciditate al unor produse cercetate este prezentat în tabelul 3.

Tabelul 3

Spectrul de aciditate al produselor cercetate

Produsul	Aciditate protonică, [mechiv/g]		Aciditate totală, [mechiv/g]	
	pK = -13,3	pK = -6,63	pK = -8,2	pK = -5,6
	77% H ₂ SO ₄	50% H ₂ SO ₄	90% H ₂ SO ₄	71% H ₂ SO ₄
N ₁	1,30	1,20	1,10	0,90
N ₃	1,40	1,30	1,20	0,80
N ₅	0,90	1,10	1,20	0,90
N ₇	0,90	1,20	1,20	1,10

Datele prezentate în tabelul 3 scot în evidență faptul că pe suprafața catalizatorilor cercetați predomină centrul acizi Brönsted puternici, care reprezintă centrul activi în reacția de alchilare.

4. Concluzii

1. Datele experimentale referitoare la evaluarea naturii și tăriei centrilor acizi subliniază importanța cationilor Ce^{3+} și La^{3+} în dezvoltarea unei acidități Brönsted pe suprafața zeoliților.
2. Studiul distribuției acidității reliefează existența pe suprafața a unor centrul acizi puternici, responsabili de activitate catalitică în reacția de alchilare.
3. Studiile viitoare vor preciza influențele cantitative ale centrilor acizi, de diferite tărie, asupra naturii produselor de reacție.

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THE ACIDE SIDE PROPERTIES OF RARE-EARTH EXCHANGED FORMS OF TYPE Y ZEOLITES

(Summary)

The acide sides properties and catalytic properties of the rare-earth cation Y zeolites, which are noted for their good structural stability and excelent catalytic activity in hydrocarbons alkylation, are studied.

LE COMPORTEMENT RHÉOLOGIQUE DES SUSPENSIONS

III. L'INFLUENCE DU COMPORTEMENT RHÉOLOGIQUE DE LA PHASE LIQUIDE SUR LE COMPORTEMENT DE LA SUSPENSION

PAR

RADU Z. TUDOSE, LIVIU POPOVICI et MARILENA BERLINSCHI

1. Introduction

Dans la littérature on indique pour les suspensions des comportements de type plastique Bingham, dilatatant et pseudoplastique. Par exemple, pour la caractérisation rhéologique des suspensions des combustibles nucléaires dans l'eau [1] ou des suspensions d'argile [2], le modèle rhéologique proposé a été celui de plastique Bingham.

En 1969, Ziegel [3] observe que l'adjonction des petites sphères en verre, dont le diamètre est d'environ 20 μm , à des différents fluides polymériques newtoniens conduit à des suspensions qui présentent un comportement rhéologique pseudoplastique.

Les suspensions des poudres de cuivre, carbone, silice dans l'eau se comportent aussi d'une manière pseudoplastique [4]...[6].

Des suspension aqueuses de bioxyde de titane ont un comportement pseudoplastique à des vitesses petites de cisaillement et un comportement dilatatant à des grandes vitesses [7].

Dans les recherches antérieures [8] avec des suspensions constituées de granules de PVC et de liquides newtoniens on a mis en évidence le comportement plastique Bingham à des concentrations allant jusqu'à 33% en phase solide et un comportement plastique non-linéaire pour des concentrations plus grandes.

Le but du présent travail est celui d'étudier l'influence du comportement rhéologique de la phase liquide, de la viscosité de la phase liquide et de la concentration de la suspension en phase solide, sur le comportement rhéologique d'une suspension.

2. Méthode expérimentale

On a utilisé des suspensions de particules de PVC, sortées, ayant un diamètre moyen de 160 μm et des concentrations de 1%, 5%, 10%, 15%, 20% en phase solide, dans des solutions aqueuses de CMC de concentrations de 1%, 2%, 3%, 4% et 5%.

Les déterminations ont été effectuées à l'aide d'un rhéoviscosimètre RHEOTEST-2, à cylindres concentriques. La température du travail a été maintenue constante à $30 \pm 0,1^\circ\text{C}$.

3. Résultats et interprétations

Les variations de la tension de cisaillement avec la vitesse de cisaillement sont présentées dans les Fig. 1...3. Si l'on analyse les courbes obtenues on peut remarquer un comportement de type plastique Bingham pour

de petites concentrations de la solution (1%, 2% CMC) sans tenir compte de la concentration de la phase solide. Pour des concentrations plus grandes (3%, 4% et 5% CMC) de la solution aqueuse en CMC, le comportement de la suspension devient pseudoplastique. Le comportement pseudoplastique est d'autant plus évident que la concentration, respectivement la viscosité de la solution est plus grande.

Pour la détermination de la concentration à partir de laquelle le comportement de type plastique Bingham se transforme en devenant pseudoplastique on a calculé les valeurs de la viscosité apparente en fonction de la vitesse de cisaillement.

Pour les concentrations de 1% et 2% CMC la viscosité apparente ne dépend pas de la vitesse de cisaillement, ce qui correspond à un comportement de type plastique Bingham. Les valeurs obtenues pour la viscosité en fonction de la concentration en CMC et PVC sont données dans le tableau 1.

Pour des valeurs de la concentration de 3%, 4% et 5% CMC la viscosité apparente baisse à mesure que la vitesse de cisaillement augmente ce qu'on peut observer en analysant les Fig. 4...6.

Tableau 1

Les valeurs de l'indice de consistance, de l'indice d'écoulement, de la viscosité apparente et du seuil de la tension pour différentes suspensions du PVC en CMC

c_{CMC} %	c_{PVC} %	K	n	$\eta \cdot 10^3$ N · s/m ²	τ_0 N/m ²
1	1	—	—	8,23	29
	5	—	—	10,65	35
	10	—	—	12,90	43
	15	—	—	16,20	50
2	20	—	—	20,10	52
	1	—	—	37,00	40
	5	—	—	45,50	41
	10	—	—	55,00	45
3	15	—	—	74,20	55
	20	—	—	91,30	60
3	1	6,37	0,662	—	0
	5	9,16	0,653	—	0
	10	15,71	0,596	—	0
	15	16,14	0,596	—	0
4	20	26,75	0,577	—	0
	1	11,72	0,699	—	0
	5	17,10	0,658	—	0
	10	23,60	0,628	—	0
5	15	31,76	0,607	—	0
	20	36,57	0,612	—	0
5	1	17,20	0,696	—	0
	5	23,51	0,675	—	0
	10	35,05	0,663	—	0
	15	42,66	0,649	—	0
5	20	52,79	0,646	—	0

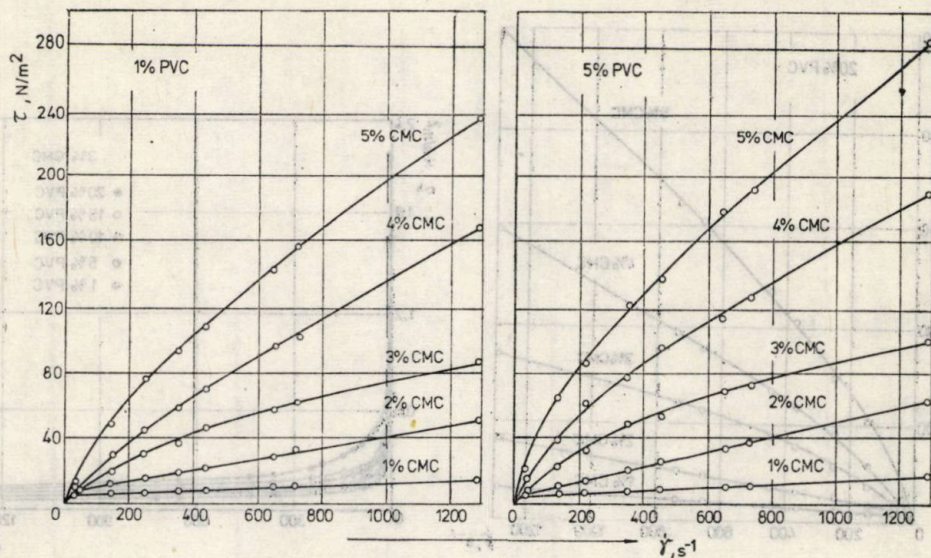


Fig. 1.—La variation de la tension de cisaillement en fonction de la vitesse de cisaillement.

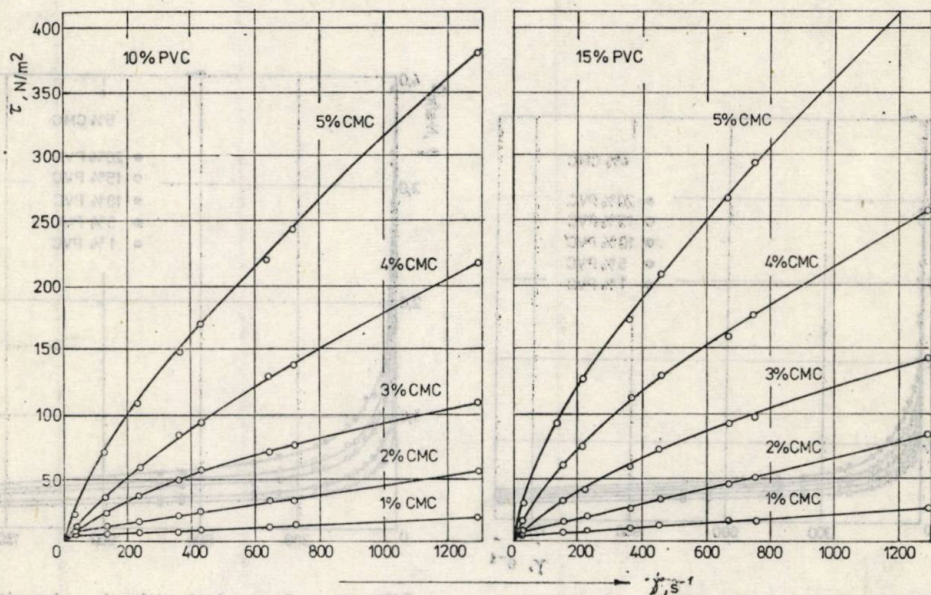


Fig. 2.—La variation de la tension de cisaillement en fonction de la vitesse de cisaillement.

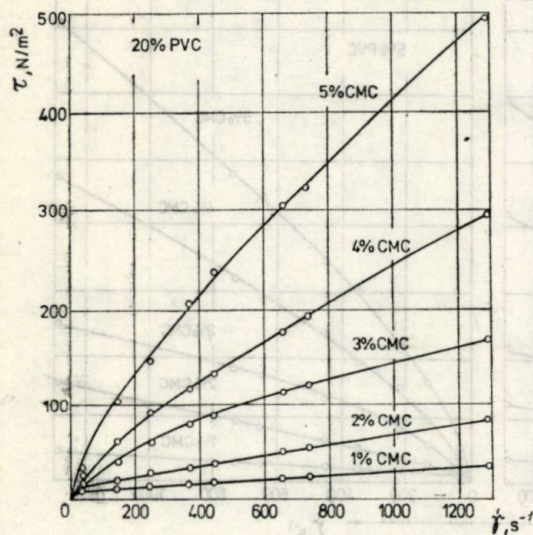


Fig. 3. — La variation de la tension de cisaillement en fonction de la vitesse de cisaillement.

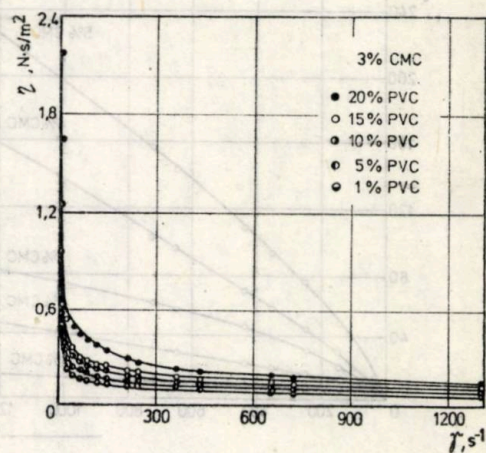


Fig. 4. — La variation de la viscosité apparente en fonction de la vitesse de cisaillement.

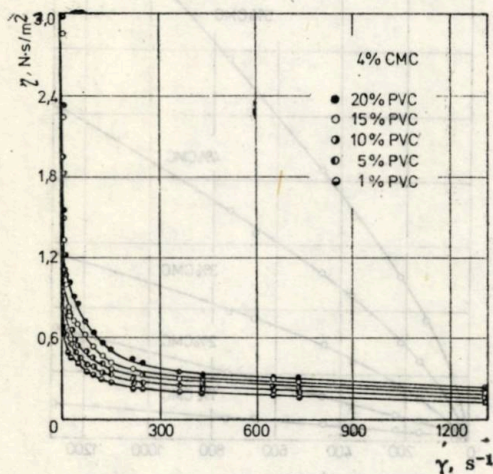


Fig. 5. — La variation de la viscosité apparente en fonction de la vitesse de cisaillement.

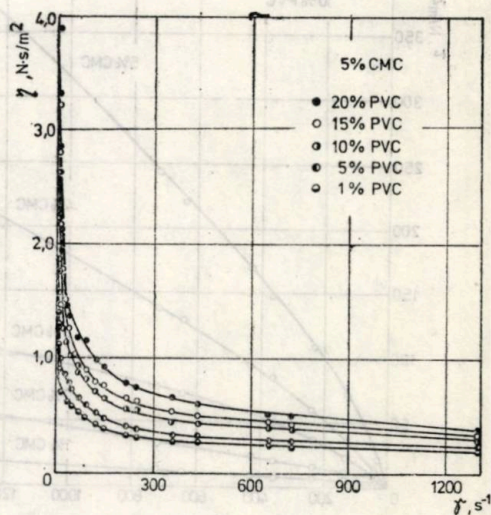


Fig. 6. — La variation de la viscosité apparente en fonction de la vitesse de cisaillement.

Si l'on compare la diminution de la viscosité pour les diverses concentrations de la phase liquide on constate que pour un même intervalle de variation de la vitesse de cisaillement, la diminution est plus accentuée à des grandes concentrations de la solution en CMC.

Afin d'établir une corrélation entre les paramètres de la sollicitation on fait appel au modèle de type plastique Bingham :

$$(1) \quad \tau - \tau_0 = \eta \dot{\gamma}$$

et au modèle de Ostwald de Waele :

$$(2) \quad \tau = K \dot{\gamma}^n$$

La linéarisation des courbes $\tau(\dot{\gamma})$ représentées dans les Fig. 2 et 3 en coordonnées logarithmiques a permis à calculer l'indice de consistance K et l'indice d'écoulement n (Tableau 1).

Analysant les valeurs inclus dans le Tableau 1 on constate que tant l'indice de consistance que l'indice d'écoulement sont fonctions de la concentration de la phase liquide et de la concentration de la phase solide.

Le sens de la variation pour les deux coefficients de matériel résulte des Fig. 7 et 8.

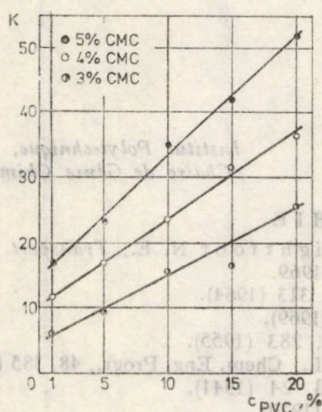


Fig. 7. — La variation de l'indice de consistance en fonction de la concentration en PVC et CMC.

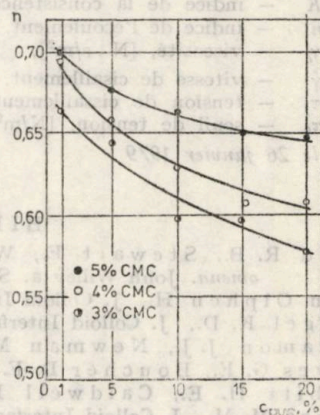


Fig. 8. — La variation de l'indice d'écoulement en fonction de la concentration en PVC et CMC.

Les résultats expérimentaux représentent les lectures effectuées immédiatement après l'introduction des solutions dans le rhéoviscosimètre pour éviter des effets de sédimentation et d'expulsion de la phase solide de l'espace du travail des cylindres de l'appareil [9].

4. Conclusions

Les recherches effectuées jusqu'à présent conduisent à la constatation que le comportement rhéologique de la suspension est influencée par le comportement rhéologique de la phase liquide et de la concentration en phase solide.

À des concentrations très petites dans la phase solide, les suspensions des liquides newtoniens présentent un comportement newtonien et, en général, vérifient l'équation d'Einstein, si les particules ont une forme sphérique [8].

Les suspensions des liquides newtoniens, pour des grandes valeurs de la concentration en phase solide, ont un comportement de type plastique Bingham, mais pour de très grandes valeurs de la concentration le comportement devient de type plastique non-linéaire [8].

Les liquides non-newtoniens à petite viscosité accusent un comportement de type plastique Bingham pour un très large intervalle de concentrations en phase solide. Dans ce cas c'est la phase solide qui est déterminante.

Les suspensions constituées de liquides non-newtoniens à grande viscosité présentent un comportement pseudoplastique pour toutes les valeurs expérimentées de la concentration en phase solide (1%...20% PVC). Dans ce dernier cas c'est la phase liquide qui est déterminante.

Notations

- c_{CMC} — concentration du CMC en phase liquide, [%],
 c_{PVC} — concentration en phase solide, [%],
 K — indice de la consistance,
 n — indice de l'écoulement,
 η — viscosité, [N · s/m²],
 $\dot{\gamma}$ — vitesse de cisaillement, [s⁻¹],
 τ — tension de cisaillement, [N/m²],
 τ_0 — seuil de tension, [N/m²].

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COMPORTAREA REOLOGICĂ A SUSPENSIILOR

III. Influența comportării reologice a fazei lichide asupra comportării suspensiilor (Rezumat)

Se urmărește modul în care este influențată comportarea reologică a unei suspensii de comportarea reologică a fazei lichide, de viscozitatea fazei lichide precum și de concentrația în fază solidă.

La concentrații foarte mici în fază solidă suspensiile cu lichide newtoniene au o comportare newtoniană, în timp ce pentru concentrații mari și foarte mari comportarea devine de tip plastic Bingham, respectiv plastic neliniară.

Lichidele nenewtoniene de viscozitate mică au o comportare de tip plastic Bingham. Suspensiile formate cu lichide nenewtoniene cu viscozitate ridicată prezintă o comportare pseudoplastică.

TRANSFER DE MASĂ CU REACȚIE CHIMICĂ NECATALITICĂ ÎN SISTEME SOLID—FLUID

I. COEFICIENȚI ECTIVI DE DIFUZIUNE*)

DE

RADU Z. TUDOSE și VIORICA NICU

1. Introducere

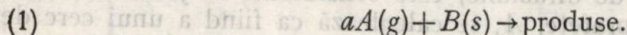
Procese elementare care stau la baza reacțiilor eterogene solid—fluid impun determinarea următoarelor mărimi: coeficientul individual de transfer de masă prin stratul limită de fluid, coeficientul efectiv de difuziune internă și viteza reacției chimice. Transferul de masă prin filmul limită exterior este un proces foarte mult studiat; pentru calculul coeficienților individuali sînt date relații criteriale [1]. Cinetica chimică pune la dispoziție suficiente metode experimentale pentru determinarea constantelor vitezei de reacție, a ordinului reacției și a energiei de activare.

Studiul difuziunii prin solide poroase se poate efectua prin mai multe metode [2], cea mai comună fiind în prezent metoda difuziunii staționare, elaborată de către Wicke și Kallenbach [3] și modificată mai tîrziu de Weisz [4]. Conform acestei metode o parte din solidul testat este plasat într-o celulă de difuziune între două fluxuri de gaze de diferite compoziții [5]. Concentrațiile curenților gazoși sînt determinate fie prin măsurători de conductivitate termică, fie prin cromatografie în gaze.

Scopul lucrării de față îl constituie prezentarea unei noi metode de determinare a coeficienților efectivi de difuziune prin tuburi capilare și medii poroase și urmărirea dependenței acestora de adîncimea de difuziune.

2. Considerații teoretice

La baza metodei propuse se află o reacție chimică ce se desfășoară cu viteză foarte mare între reactantul gazos al cărui coeficient de difuziune urmează a fi determinat și un reactant solid, care poate fi diferit de cel din procesul solid—fluid studiat, dar care trebuie să îndeplinească condiția de a-și schimba culoarea după reacție. Forma generală a procesului chimic este:



Reactantul solid (B) va fi dizolvat într-un solvent și depus pe pereții interiori ai unui tub capilar sau pe suprafața unor granule inerte ce formează

*) Comunicare prezentată la sesiunea științifică a Institutului de petrol și gaze, Ploiești, 1978.

un strat sau prin îmbibarea unei granule poroase. Se îndepărtează apoi complet solventul utilizat. În prealabil proba se umectează într-un spațiu saturat cu vapori și se aduce în contact cu faza gazoasă ce conține reactantul gazos (A). Acesta difuzează spre interior, reacționând cu solidul.

Principiul determinării se bazează pe urmărirea deplasării suprafeței de reacție în timp, $l_c(t)$ (fig. 1). Pentru fiecare experiment sînt cunoscuți următorii parametri de lucru: concentrația reactantului fluid, concentrația reactantului solid, dimensiunile capilarei, temperatura și evoluția frontului de reacție în timp.

Fluxul de difuziune a reactantului gazos, conform legii lui Fick, este :

$$(2) \quad N_A = -D_{Ac} \frac{dC_A}{dl}$$

sau în cazul unei suprafețe aflată la distanța Δl_c de capătul tubului ($\Delta l_c = \delta_c$) :

$$(2') \quad N_A = D_{Ac} \frac{\Delta C_A}{\Delta l_c}$$

unde :

$$(3) \quad N_A = \frac{n_A}{A \Delta t}$$

Din ultimele două ecuații rezultă :

$$(4) \quad D_{Ac} = \frac{n_A}{A \Delta t} \cdot \frac{\Delta l_c}{\Delta C_A}$$

Relația (4) este folosită în calculul coeficientului efectiv de difuziune a fluidului A .

Mărimile care intervin în ecuația (4) se calculează din datele experimentale.

Cantitatea de fluid (n_A , moli) ce difuzează prin suprafața A în intervalul de timp Δt se determină în modul următor : se împarte tubul de lungime L în n segmente egale, fiecare de înălțime Δl . Cunoscînd cantitatea totală de reactant solid depus în strat uniform în interiorul tubului, prin împărțirea acesteia la n se află cantitatea de reactant solid, n_B , depusă pe porțiunea Δl a tubului. Reactantul gazos ce difuzează pe lungimea Δl în intervalul Δt reacționează cu solidul depus aici, deci, conform reacției (1), încît $n_A = an_B$.

Gradientul de concentrație, ΔC_A , pe distanța Δl_c este $\Delta C_A = C_{A0} - 0 = C_{A0}$ (concentrația de reactant A în fază gazoasă rămîne constantă).

Suprafața prin care are loc difuziunea (respectiv punctul pentru care se calculează coeficientul de difuziune) este considerată la jumătatea distanței Δl . Aria acestei suprafețe, A , se calculează ca fiind a unui cerc de rază egală cu raza tubului, din care se scade grosimea stratului de reactant solid depus.

Intervalul de timp Δt este cel corespunzător din grafic (fig. 1) lui Δl , iar Δl_c reprezintă tocmai poziția în care se calculează coeficientul de difuziune (δ_c).

Determinînd coeficientul efectiv de difuziune, D_{Ac} , la diverse distanțe față de curentul gazos, δ_c , se poate trasa curba $D_{Ac} = f(\delta_c)$.

Reacția (1) are loc cu o viteză foarte mare, mult mai mare decît cea a procesului de difuziune internă, astfel că modelul ce descrie desfășurarea

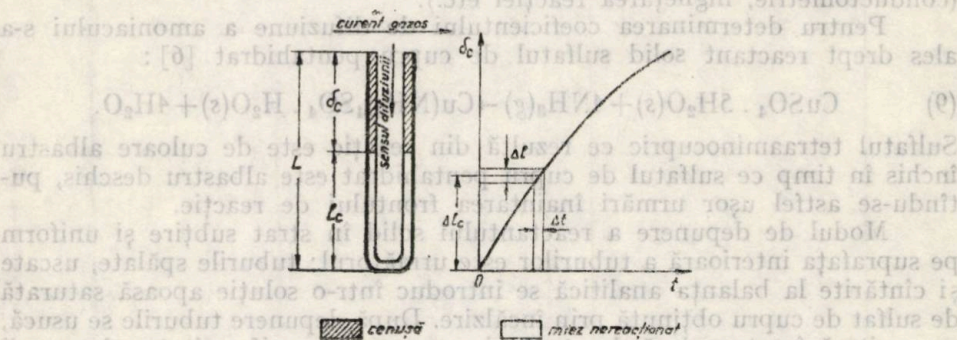


Fig. 1. — Difuziunea în capilară.

acestui proces este cel eterogen [2], care conduce, pentru timpul de conversie adimensional, la relația :

$$(5) \quad \tau = 1 - \lambda_c + \frac{K_{T4,c}^2}{L} (1 - \lambda_c) \left(1 + \frac{1}{K_{Sh,c}} \right) - \frac{K_{T4,c}^2}{2L} (1 - \lambda_c^2).$$

Cînd rezistența la difuziune prin filmul limită exterior este neglijabilă ($K_{Sh,c} \rightarrow \infty$) și ținînd cont că viteza de reacție este foarte mare ($k_s \rightarrow \infty$) se obține :

$$(6) \quad t = \frac{aC_{B0}L^2}{D_{Ac}C_{A0}} (1 - \lambda_c) - \frac{aC_{B0}L^2}{2C_{A0}D_{Ac}} (1 - \lambda_c^2).$$

Conversia reactantului solid pentru modelul eterogen se calculează cu relația simplă :

$$(7) \quad X = \frac{A(L - l_c)}{AL} = 1 - \lambda_c,$$

ceea ce permite scrierea relației (7) într-o formă simplificată și anume :

$$(8) \quad t = \frac{aC_{B0}L^2X^2}{2C_{A0}D_{Ac}}.$$

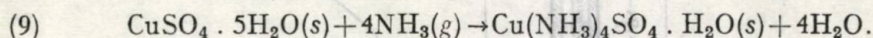
Determinînd experimental $X(t)$ se poate calcula cu ajutorul ecuației (8) coeficientul efectiv de difuziune, D_{Ac} și compara cu valoarea găsită prin metoda propusă, la aceiași parametri de lucru.

3. Tehnica experimentală

Principala problemă referitoare la determinarea coeficienților efectivi de difuziune prin metoda propusă o constituie găsirea unui reactant solid cu care reactantul gazos, al cărui coeficient se calculează, să reac-

ționeze cu o viteză foarte mare (practic instantaneu) și produsul obținut să fie de culoare diferită de cea a componentului solid inițial. Cea de a doua condiție nu este absolut obligatorie dar ea simplifică considerabil tehnica de urmărire a avansării reacției, evitând folosirea unor metode mai dificile (conductometrie, înghețarea reacției etc.).

Pentru determinarea coeficientului de difuziune a amoniacului s-a ales drept reactant solid sulfatul de cupru pentahidrat [6]:



Sulfatul tetraaminocupric ce rezultă din reacție este de culoare albastru închis în timp ce sulfatul de cupru pentahidrat este albastru deschis, putându-se astfel ușor urmări înaintarea frontului de reacție.

Modul de depunere a reactantului solid în strat subțire și uniform pe suprafața interioară a tuburilor este următorul: tuburile spălate, uscate și cântărite la balanța analitică se introduc într-o soluție apoasă saturată de sulfat de cupru obținută prin încălzire. După depunere tuburile se usucă, cu o viteză foarte redusă, la etuvă și se urmărește uniformitatea depunerii folosind o lupă, îndepărtând probele necorespunzătoare. După uscare tuburile se țin în atmosferă saturată cu vapori de apă timp de 24 ore pentru ca sulfatul de cupru anhidru (datorită uscării la etuvă) să absoarbă apa necesară desfășurării reacției (9). Tuburile astfel obținute se cântăresc din nou la balanța analitică după care se amplasează într-un circuit gazos, ce conține componentul al cărui coeficient de difuziune urmărim să-l determinăm. Sistemul experimental permite reglarea temperaturii, a concentrației în component gazos precum și a vitezei de deplasare a amestecului de gaze.

Marcind momentul atașării probei la sistemul gazos se urmărește înaintarea în timp a frontului de reacție.

Coeficientul de difuziune a amoniacului în mediu poros se determină folosind nisip cuarțos. În acest scop se cântărește, la balanța analitică, cantitatea de nisip cuarțos care încapă într-un tub de sticlă. Se introduce nisipul într-o soluție de sulfat de cupru. După depunere se usucă la etuvă, se ține în atmosferă de vapori de apă timp de 24 ore, după care se introduce în tub și se recântărește, rezultând prin diferență cantitatea de reactant solid depusă. Tubul cu nisip cuarțos se atașează la aceeași instalație ca și capilarele și se urmărește înaintarea suprafeței de reacție în strat. Tehnica de calcul este aceeași.

4. Rezultate experimentale

S-au efectuat determinări în diferite condiții, variind concentrația reactantului solid ($1 \cdot 10^{-4}$... $20 \cdot 10^{-4}$ mol/ml), concentrația reactantului gazos ($1 \cdot 10^{-6}$... $5 \cdot 10^{-6}$ mol/ml), diametrul tuburilor (0,5...7 mm) și lungimea lor (10...50 mm). Temperatura de lucru a fost de 18°C.

Astfel, pentru un tub cu diametrul de 1,5 mm, având lungimea de 50 mm, concentrația amoniacului în curentul gazos, $C_{A0} = 4.411 \cdot 10^{-6}$ mol/ml, concentrația reactantului solid $C_{B0} = 3,02 \cdot 10^{-4}$ mol/ml (ml — volumul tubului), grosimea zonei de cenușă variază în timp după cum indică fig. 2.

Cantitatea de sulfat de cupru pentahidrat depusă pe întreg tubul este de 0,0065 g. Se împarte tubul în cinci segmente egale ($\Delta l = 10$ mm), încît pe fiecare segment Δl este depusă a cincia parte din cantitatea totală (n_B).

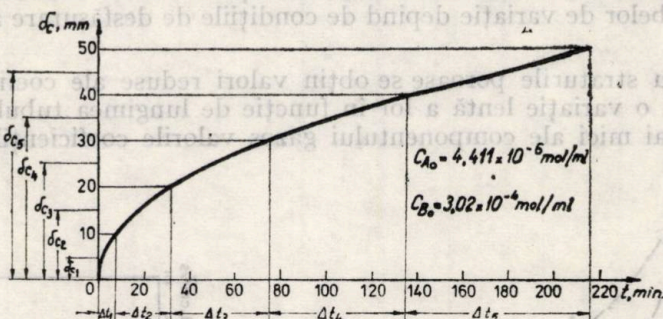


Fig. 2. — Avansarea frontului de reacție.

Cantitatea de amoniac care difuzează pe lungimea Δl va fi $n_A = 4n_B \times (2,132 \cdot 10^{-5} \text{ mol})$.

Aria suprafeței de difuziune, cunoscînd raza tubului corectată în funcție de grosimea stratului de sulfat de cupru depus, este de $1,708 \cdot 10^{-6} \text{ m}^2$.

Gradientul de concentrație rezultă $\Delta C_A = C_{A0} = 4,411 \text{ mol/m}^3$.

Datele de mai sus, înlocuite în relația (4), conduc la valorile coeficientului de difuziune prezentate în fig. 3.

Trasînd, pe baza datelor experimentale, graficul $X(t)$ (fig. 4 a) și aplicînd modelul eterogen (ecuația (8)) se obține pentru variația coeficientului de difuziune în funcție de lungime curba reprezentată în fig. 4 b.

Apropierea datelor obținute pe baza modelului eterogen de cele rezultate prin metoda propusă constituie o verificare a exactității ei.

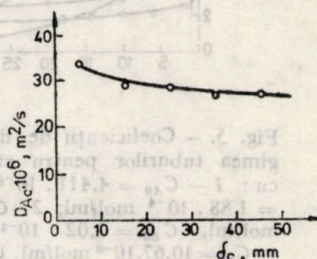


Fig. 3. — Variația coeficientului de difuziune obținut experimental, pe direcția difuziunii; $C_{A0} = 4,411 \cdot 10^{-5} \text{ mol/ml}$; $C_{B0} = 3,02 \cdot 10^{-4} \text{ mol/ml}$.

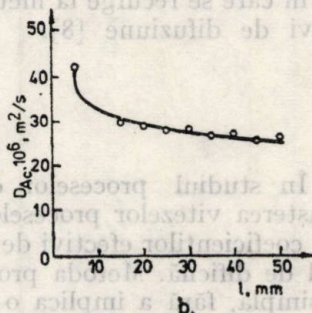
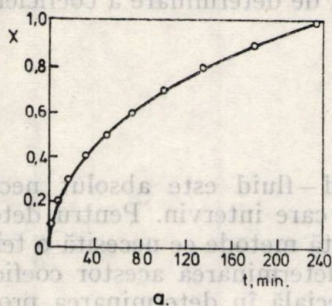


Fig. 4. — Determinarea coeficientului de difuziune a amoniacului pe baza modelului eterogen de desfășurare a reacțiilor necatalitice solid—fluid: a — variația conversiei reactantului solid în timp; b — variația coeficientului de difuziune pe direcția difuziunii.

5. Discuții

Coeficienții de difuziune scad în direcția difuziei. Valorile lor precum și alura curbelor de variație depind de condițiile de desfășurare a procesului (fig. 5).

Pentru straturile poroase se obțin valori reduse ale coeficienților de difuziune și o variație lentă a lor în funcție de lungimea tubului. La concentrații mai mici ale componentului gazos valorile coeficienților de difuziune cresc.

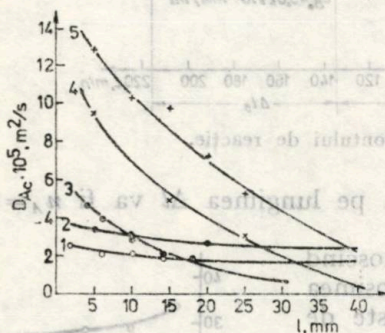


Fig. 5. — Coeficienții de difuziune pe lungimea tuburilor pentru strat de granule cu: 1 — $C_{A0} = 4,411 \cdot 10^{-6}$ mol/ml, $C_{B0} = 1,88 \cdot 10^{-4}$ mol/ml; 2 — $C_{A0} = 4,411 \cdot 10^{-6}$ mol/ml, $C_{B0} = 3,02 \cdot 10^{-4}$ mol/ml; 3 — $C_{A0} = 10,67 \cdot 10^{-6}$ mol/ml, $C_{B0} = 1,276 \cdot 10^{-4}$ mol/ml; 4 — $C_{A0} = 3,25 \cdot 10^{-6}$ mol/ml, $C_{B0} = 4,744 \cdot 10^{-4}$ mol/ml; 5 — $C_{A0} = 0,956 \cdot 10^{-6}$ mol/ml, $C_{B0} = 1,451 \cdot 10^{-4}$ mol/ml.

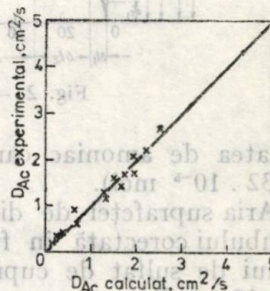


Fig. 6. — Compararea coeficienților de difuziune experimentali și calculați.

Abaterile valorilor experimentale ale coeficienților de difuziune, obținute aplicând metoda propusă, în raport cu valorile calculate pe baza modelului eterogen (fig. 6) sînt în general mai mici decît cele ce apar în cazul în care se recurge la metoda staționară de determinare a coeficienților efectivi de difuziune [8].

6. Concluzii

În studiul proceselor eterogene solid—fluid este absolut necesară cunoașterea vitezelor proceselor elementare care intervin. Pentru determinarea coeficienților efectivi de difuziune există metode ce necesită o tehnică destul de dificilă. Metoda propusă pentru determinarea acestor coeficienți este simplă, fără a implica o aparatură specială în determinarea propriu-zisă și conduce la rezultate satisfăcătoare. Compararea valorilor experimentale cu cele obținute pe baza modelului eterogen confirmă valabilitatea metodei propuse.

Notații

- a — coeficient stoechiometric adimensional,
 A — suprafața de difuziune, $[L^2]$,
 C_A — concentrația reactantului gazos, $[mol/L^3]$,
 C_{A0} — concentrația reactantului în masa fazei gazoase,
 C_B — concentrația reactantului solid, $[mol/L^3]$,
 C_{B0} — concentrația inițială a reactantului solid,
 D_{Ac} — coeficient efectiv de difuziune, $[L^2/\theta]$,
 h_{tA} — coeficient de transfer de masă prin stratul limită exterior,
 k_s — constanta vitezei de reacție raportată la suprafață, $[L^2/mol]$,
 k_v — constanta vitezei de reacție raportată la volum, $[L^3/mol]$,
 $K_{Sh,c} = h_{tA} L / D_{Ac}$ — numărul de comparație Sherwood pentru zona de cenușă, [adimensional],
 $K_{Ti,s} = L \sqrt{a k_s C_{B0} / D_{Ac}}$ — numărul de comparație Thiele pentru zona de cenușă, [adimensional],
 l_s — distanța în direcția difuziunii, $[L]$,
 l_c — grosimea miezului nereacționat, $[L]$,
 L — dimensiunea solidului sau lungimea capilarei, $[L]$,
 N_A — fluxul de difuziune a componentului fluid, $[mol/L^2\theta]$,
 n_A — cantitatea de component fluid, $[mol]$,
 n_B — cantitatea de component solid, $[mol]$,
 t — timp, $[\theta]$,
 X — conversia reactantului solid, [adimensional],
 δ_s — grosimea zonei de cenușă, $[L]$,
 $\lambda_c = l_c / L$ — adimensional,
 τ — timp [adimensional].

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Institutul politehnic, Iași,
Catedra de inginerie chimică

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MASS TRANSFER WITH NONCATALYTIC HETEROGENEOUS SOLID—FLUID REACTIONS

I. Effective Diffusion Coefficients

(Summary)

The external diffusion, the internal diffusion or the chemical reaction may be the rate-controlling factor for many solid—fluid reactions. Having in mind that the internal diffusion is rate controlling for the processes with very grate reaction rate, a method and a installation have been conceived for determination of the effective diffusion coefficients and their variation with the penetration depth.

Notatii

- k — coeficient stoichiometric adimensional;
 k_d — suprafata de difuziune, $[L^2]$;
 C_{d0} — concentratia reactantului gazeos, $[mol/L^3]$;
 C_{d0} — concentratia reactantului in masa lazei gazease;
 C_{s0} — concentratia reactantului solid, $[mol/L^3]$;
 C_{s0} — concentratia initiala a reactantului solid;
 D_{d0} — coeficient efectiv de difuziune, $[L^2/t]$;
 k_{d0} — coeficient de transfer de masa prin starea limita externa;
 k_s — constanta vitezei de reactie raportata la suprafata, $[L^2/mol]$;
 k_v — constanta vitezei de reactie raportata la volum, $[L^3/mol]$;
 k_{v0} — numarul de comparatie Sherwood pentru zona de cenus;
 $[adimensional]$
 K_{v0} — $[L^3/C_{d0} D_{d0}]$ — numarul de comparatie Thiele pentru zona de cenus, $[adimensional]$;
 L — distanta la directia difuziunii, $[L]$;
 L_0 — grosimea miezului necatalizat, $[L]$;
 L_0 — dimensiunea solidului sau lungimea capetelui, $[L]$;
 N_d — fluxul de difuziune a componentului fluid, $[mol/L^2 t]$;
 n_d — cantitatea de component fluid, $[mol]$;
 n_s — cantitatea de component solid, $[mol]$;
 t — timp, $[t]$;
 Y — conversia reactantului solid, $[adimensional]$;
 Y_0 — grosimea zonei de cenus, $[L]$;
 $Y_0 = L_0/L$ — adimensional;
 τ — timp $[adimensional]$.

Institutul Politehnic, Iasi
 Catedra de Inginerie Chimica

Primita la 30 aprilie 1979

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MASS TRANSFER WITH NONCATALYTIC HETEROGENEOUS SOLID-FLUID

REACTIONS

1. Effective Diffusion Coefficients

(Summary)

The external diffusion, the internal diffusion or the chemical reaction may be the rate controlling factor for many solid-fluid reactions. Having in mind that the internal diffusion is rate controlling for the processes with very small reaction rates, a method and a installation have been conceived for determination of the effective diffusion coefficients and their variation with the penetration depth.

EFICIENȚA UTILIZĂRII DREPT COMBUSTIBIL A GAZELOR DE PURJĂ DIN INSTALAȚIILE DE AMONIAC^{*)}

DE

C. CALISTRU și ILIE SIMINICEANU

1. Introducere

În instalațiile de obținere a amoniacului gazul metan este utilizat atât ca materie primă (gaz metan tehnologic) cit și ca gaz combustibil în cuptorul de reformare precum și la cazanul auxiliar, la producerea aburului.

Structura consumului de gaz metan într-o linie industrială modernă care produce 2 263,2 kmol amoniac/h (925 t/24 h) este prezentată în tabelul 1.

Utilizarea rațională, eficientă, a gazului metan, impune diminuarea ponderii gazului de combustie și reducerea coeficienților de consum de gaz tehnologic. În lucrări anterioare s-a elaborat o metodă de determinare a consumului minim de gaz metan combustibil în cuptorul de reformare primară bazată pe optimizarea bilanțului termic în procesul global de reformare [1] precum și metode de reducere a coeficienților de consum de materii prime [2]. În literatură pot fi semnalate, de asemenea, preocupări în direcția reducerii consumului de energie în fabricile de amoniac, prin modificarea procesului tehnologic [3].

Tabelul 1

Structura consumului de gaz metan într-o instalație modernă de 925 t/24 h NH_3

Cantitatea	kmol/h	Nm ³ /h	kg/h	%
Tipul de consum				
Gaz tehnologic	1 103,9	24 727,36	17 662,4	64,22
Gaz combustibil cuptor	427,5	9 576,00	6 840,0	24,87
Gaz combustibil cazan	187,5	4 200,00	3 000,0	10,91
Total	1 718,9	38 503,36	27 502,4	100,00

^{*)} Prezentată la Simpozionul cu tema „Preocupări și rezultate obținute în proiectarea, execuția și exploatarea instalațiilor și utilajelor din industria chimică, în scopul reducerii importurilor, a consumului de metal și energie” I.I.T.P.I.C., Sibiu, 17–18 octombrie 1979.

În această lucrare se studiază posibilitatea reducerii consumului de gaz metan combustibil prin înlocuirea parțială a acestuia cu gaze de purjă, gaze deșeu din bucla de sinteză a amoniacului. În tabelul 2 este redată compoziția gazelor de purjă rezultate în ciclul de sinteză al unei fabrici de 925 t NH_3 /24 h.

Tabelul 2

Compoziția prescrisă a gazelor de purjă

Compoziție \ Component	Hydrogen	Metan	Amoniac	Azot	Argon	Total
Nm^3/h	1 746,49	737,50	3,274	561,64	225,96	3 274,86
kmol/h	77,96	32,92	0,45	25,07	10,08	146,18
kg/h	$\bar{M} = 12,19 \text{ kg/kmol}$					891,37
% vol.	53,33	22,52	0,10	17,15	6,90	100,00

Aceste gaze conțin peste 73% substanțe combustibile (H_2 , CH_4 , NH_3). Pe baza datelor din tabelele 1 și 2 se observă că gazele de purjă nu pot înlocui total gazul metan de ardere, de aceea apare problema determinării fracției de gaz metan ce se poate economisi prin utilizarea acestor gaze deșeu la ardere. Pe de altă parte cantitatea și calitatea gazelor de purjă variază de la o instalație la alta cât și în cadrul aceleiași instalații. În tabelul 3 se prezintă variația compoziției gazelor de purjă din instalația „S” de la C. C. Slobozia, pe o perioadă de 10 zile.

Tabelul 3

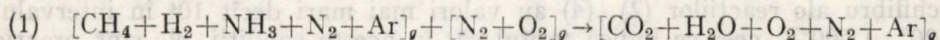
Variația compoziției gazelor de purjă

Component	Ziua										Media %
	1	2	3	4	5	6	7	8	9	10	
NH_3	0,80	0,67	0,68	0,64	0,80	0,50	0,24	0,50	0,94	0,64	0,641
CH_4	11,30	15,43	13,20	10,50	15,25	12,00	16,75	12,00	11,80	12,80	13,103
H_2	63,51	54,63	57,21	61,66	56,50	56,00	59,18	56,05	60,54	58,36	58,310
N_2	20,65	24,70	24,60	23,00	20,25	19,65	20,65	22,25	24,20	24,20	22,415
Ar	3,74	4,57	4,30	3,70	4,35	3,74	4,18	3,74	4,05	4,00	4,032

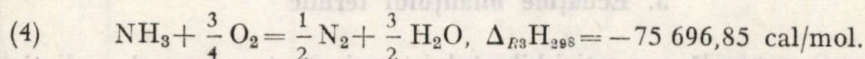
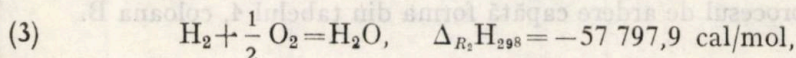
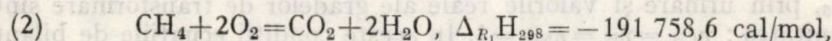
Datorită variațiilor compoziției gazelor de purjă precum și ale parametrilor tehnologici ai procesului de reformare este necesară stabilirea unui model matematic care să permită determinarea consumului de gaz combustibil în orice condiții.

2. Ecuatiile bilanțului de masă în procesul de ardere a gazelor de purjă

Procesul de ardere a gazelor de purjă se definește stoichiometric prin ecuația caracteristică:



și ecuațiile stoichiometrice:



Tabelul 4

Ecuatiile de bilanț de masă în procesul de ardere a gazelor de purjă

A. Forma generală	B. Forma particulară
$n_{\text{CH}_4} = n_{\text{CH}_4}^0 - n_{\text{CH}_4}^0 \eta_{\text{CH}_4}$	$n_{\text{CH}_4} = 0$
$n_{\text{H}_2} = n_{\text{H}_2}^0 - n_{\text{H}_2}^0 \eta_{\text{H}_2}$	$n_{\text{H}_2} = 0$
$n_{\text{NH}_3} = n_{\text{NH}_3}^0 - n_{\text{NH}_3}^0 \eta_{\text{NH}_3}$	$n_{\text{NH}_3} = 0$
$n_{\text{O}_2} = n_{\text{O}_2}^0 - 2n_{\text{CH}_4}^0 \eta_{\text{CH}_4} - \frac{1}{2}n_{\text{H}_2}^0 \eta_{\text{H}_2} - \frac{3}{4}n_{\text{NH}_3}^0 \eta_{\text{NH}_3}$	$n_{\text{O}_2} = n_{\text{O}_2}^0 - 2n_{\text{CH}_4}^0 - \frac{1}{2}n_{\text{H}_2}^0 - \frac{3}{4}n_{\text{NH}_3}^0$
$n_{\text{H}_2\text{O}} = 2n_{\text{CH}_4}^0 \eta_{\text{CH}_4} + n_{\text{H}_2}^0 \eta_{\text{H}_2} + \frac{3}{2}n_{\text{NH}_3}^0 \eta_{\text{NH}_3}$	$n_{\text{H}_2\text{O}} = 2n_{\text{CH}_4}^0 + n_{\text{H}_2}^0 + \frac{3}{2}n_{\text{NH}_3}^0$
$n_{\text{CO}_2} = n_{\text{CH}_4}^0 \eta_{\text{CH}_4}$	$n_{\text{CO}_2} = n_{\text{CH}_4}^0$
$n_{\text{N}_2} = n_{\text{N}_2}^0 + \frac{1}{2}n_{\text{NH}_3}^0 \eta_{\text{NH}_3}$	$n_{\text{N}_2} = n_{\text{N}_2}^0 + \frac{1}{2}n_{\text{NH}_3}^0 \eta_{\text{NH}_3}$
$n_{\text{Ar}} = n_{\text{Ar}}^0$	$n_{\text{Ar}} = n_{\text{Ar}}^0$
$n_T = n_T^0 \left(1 - \frac{1}{2}X_{\text{H}_2}^0 \eta_{\text{H}_2} + \frac{1}{4}X_{\text{NH}_3}^0 \eta_{\text{NH}_3} \right)$	$n_T = n_T^0 \left(1 - \frac{1}{2}X_{\text{H}_2}^0 + \frac{1}{4}X_{\text{NH}_3}^0 \right)$

Gradele de transformare ale metanului (η_{CH_4}), hidrogenului (η_{H_2}) și amoniacului (η_{NH_3}), în reacțiile (2)...(4), se definesc prin relațiile:

$$(5) \quad \eta_{\text{CH}_4} = \frac{n_{\text{CH}_4}^{01} - n_{\text{CH}_4}^1}{n_{\text{CH}_4}^{01}} = \frac{n_{\text{O}_2}^{01} - n_{\text{O}_2}^1}{2n_{\text{CH}_4}^{01}} = \frac{n_{\text{CO}_2}^1}{n_{\text{CH}_4}^{01}} = \frac{n_{\text{H}_2\text{O}}^1}{2n_{\text{CH}_4}^{01}},$$

$$(6) \quad \eta_{\text{H}_2} = \frac{n_{\text{H}_2}^{02} - n_{\text{H}_2}^2}{n_{\text{H}_2}^{02}} = \frac{n_{\text{O}_2}^{02} - n_{\text{O}_2}^2}{n_{\text{H}_2}^{02}/2} = \frac{n_{\text{H}_2\text{O}}^2}{n_{\text{H}_2}^{02}},$$

$$(7) \quad \eta_{\text{NH}_3} = \frac{n_{\text{NH}_3}^{\text{O}_3} - n_{\text{NH}_3}^3}{n_{\text{NH}_3}^{\text{O}_3}} = \frac{n_{\text{O}_2}^{\text{O}_3} - n_{\text{O}_2}^3}{3n_{\text{NH}_3}^{\text{O}_3}/4} = \frac{n_{\text{N}_2}^3 - n_{\text{N}_2}^{\text{O}_3}}{n_{\text{NH}_3}^{\text{O}_3}/2} = \frac{n_{\text{H}_2\text{O}}^3 - n_{\text{H}_2\text{O}}^{\text{O}_3}}{3n_{\text{NH}_3}^{\text{O}_3}/2}.$$

Pe baza relațiilor (5)...(7) și a ecuațiilor de concretizare se obține modelul matematic de bilanț de masă în forma generală. Constantele de echilibru ale reacțiilor (2)...(4) au valori mai mari decât 10^4 în intervalul $500^\circ \dots 1500^\circ \text{K}$, ceea ce indică faptul că, în aceste condiții, ele sînt practic totale [4]. Analiza gazelor de ardere nu indică prezența reactanților CH_4 , H_2 și NH_3 , prin urmare și valorile reale ale gradelor de transformare sînt egale cu unitatea: $\eta_{\text{CH}_4} = \eta_{\text{H}_2} = \eta_{\text{NH}_3} = 1$. În aceste condiții ecuațiile de bilanț de masă în procesul de ardere capătă forma din tabelul 4, coloana B.

3. Ecuațiile bilanțului termic

Forma generală a ecuației bilanțului termic pentru „zona de radiație” a cuptorului de reformare primară a metanului este:

$$(8) \quad \Delta H_0 + \Delta H_R = \Delta H + \Delta H_{\text{ex}}.$$

Termenii ecuației (8) se detaliază, conform ecuațiilor (1)...(4), astfel:

$$(9) \quad \Delta H_0 = n_{g.p.}^0 \left[\sum_{i=1}^5 X_i^0 \int_{298}^{T_{01}} C_{pi} dT + \dot{X}_{\text{aer}}^0 \int_{298}^{T_{02}} C_{paer} dT \right],$$

unde: $i = \text{CH}_4, \text{H}_2, \text{NH}_3, \text{N}_2, \text{Ar}$ iar $C_{paer} = 0,21 C_{p\text{O}_2} + 0,79 C_{p\text{N}_2}$.

Raportul molar inițial $\dot{X}_{\text{aer}}^0 = n_{\text{aer}}^0 / n_{g.p.}^0$ se poate determina cu ajutorul relației:

$$(10) \quad \dot{X}_{\text{aer}}^0 = 4,762 \varphi \left(2X_{\text{CH}_4}^0 + \frac{1}{2} X_{\text{H}_2}^0 + \frac{3}{4} X_{\text{NH}_3}^0 \right).$$

Ecuația (10) exprimă, deci, dependența:

$$(11) \quad \Delta H_0 = n_{g.p.}^0 \cdot F(T_{01}, T_{02}, X_{\text{CH}_4}^0, X_{\text{H}_2}^0, X_{\text{NH}_3}^0, X_{\text{N}_2}^0, \varphi) = n_{g.p.}^0 \cdot X.$$

Funcția X se concretizează, după integrare, utilizînd datele din tabelul 5, fiind de forma:

$$(12) \quad X = A_0 + B_0 T_{01} + C_0 T_{01}^2 + D_0 T_{01}^3 + \dot{X}_{\text{aer}}^0 (6,2643 T_{02} + 1,032494 \cdot 10^{-3} T_{02}^2 - 0,14727 \cdot 10^{-6} T_{02}^3),$$

unde:

$$(13) \quad \begin{cases} A_0 = -1\,775,37 X_{\text{CH}_4}^0 - 2\,055,63 X_{\text{H}_2}^0 - 2\,471,98 X_{\text{NH}_3}^0 - \\ \quad - 1\,955,12 X_{\text{N}_2}^0 - 1\,480,3 X_{\text{Ar}}^0 - 1\,954,5 \dot{X}_{\text{aer}}^0, \\ B_0 = 3,422 X_{\text{CH}_4}^0 + 6,88 X_{\text{H}_2}^0 + 8,04 X_{\text{NH}_3}^0 + 6,3 X_{\text{N}_2}^0 + 4,967 X_{\text{Ar}}^0, \\ C_0 = (8,9225 X_{\text{CH}_4}^0 + 0,033 X_{\text{H}_2}^0 + 0,35 X_{\text{NH}_3}^0 + 0,9095 X_{\text{N}_2}^0) \cdot 10^{-3}, \\ D_0 = (-1,3883 X_{\text{CH}_4}^0 + 0,093 X_{\text{H}_2}^0 + 1,7 X_{\text{NH}_3}^0 - 0,115 X_{\text{N}_2}^0) \cdot 10^{-6}. \end{cases}$$

Termenul ΔH se exprimă, în mod analog, sub forma :

$$(14) \quad \Delta H = \sum_{i=1}^5 n_i \int_{298}^T C_{pi} dT,$$

unde : $i = \text{CO}_2, \text{H}_2\text{O}, \text{O}_2, \text{N}_2, \text{Ar}$.

Pe baza ecuațiilor de bilanț de masă, forma B, relația (14) devine:

$$(14') \quad \Delta H = n_{g.p.}^0 \left[X_{\text{CH}_4}^0 \int_{298}^T (C_{p\text{CO}_2} + 2C_{p\text{H}_2\text{O}} - 2C_{p\text{O}_2}) dT + \right. \\ \left. + X_{\text{H}_2}^0 \int_{298}^T \left(C_{p\text{H}_2\text{O}} - \frac{1}{2} C_{p\text{O}_2} \right) dT + X_{\text{NH}_3}^0 \int_{298}^T \left(\frac{3}{2} C_{p\text{H}_2\text{O}} - \frac{3}{4} C_{p\text{O}_2} + \frac{1}{2} C_{p\text{N}_2} \right) dT + \right. \\ \left. + X_{\text{N}_2}^0 \int_{298}^T C_{p\text{N}_2} dT + X_{\text{Ar}}^0 \int_{298}^T C_{p\text{Ar}} dT + \dot{X}_{\text{aer}}^0 \int_{298}^T C_{p\text{aer}} dT \right].$$

Ecuația (14') exprimă dependența :

$$(15) \quad \Delta H = n_{g.p.}^0 F(X_{\text{CH}_4}^0, X_{\text{H}_2}^0, X_{\text{NH}_3}^0, X_{\text{N}_2}^0, \varphi, T) = n_{g.p.}^0 Z.$$

După înlocuirea mărimilor din tabelul 5 și integrare, funcția Z capătă forma :

$$(16) \quad Z = A'_0 + B'_0 T + C'_0 T^2 + D'_0 T^3,$$

unde :

$$(17) \quad \left\{ \begin{aligned} A'_0 &= -2885,49 X_{\text{CH}_4}^0 - 1219,77 X_{\text{H}_2}^0 - 2807,22 X_{\text{NH}_3}^0 - 1955,13 X_{\text{N}_2}^0 - \\ &\quad - 1480,31 X_{\text{Ar}}^0 - 1955,55 \dot{X}_{\text{aer}}^0, \\ B'_0 &= 8,37 X_{\text{CH}_4}^0 + 3,825 X_{\text{H}_2}^0 + 8,8875 X_{\text{NH}_3}^0 + 6,30 X_{\text{N}_2}^0 + 4,9675 X_{\text{Ar}}^0 + \\ &\quad + 6,2643 \dot{X}_{\text{aer}}^0, \\ C'_0 &= (4,5595 X_{\text{CH}_4}^0 + 0,894 X_{\text{H}_2}^0 + 1,79577 X_{\text{NH}_3}^0 + 0,90955 X_{\text{N}_2}^0 + \\ &\quad + 1,032494 \dot{X}_{\text{aer}}^0) \cdot 10^{-2}, \\ D'_0 &= (-0,51633 X_{\text{CH}_4}^0 + 0,02 X_{\text{H}_2}^0 - 0,0275 X_{\text{NH}_3}^0 - 0,115 X_{\text{N}_2}^0 - \\ &\quad - 0,14725 \dot{X}_{\text{aer}}^0) \cdot 10^{-6}. \end{aligned} \right.$$

Termenul ΔH_R se determină cu relația :

$$(18) \quad \Delta H_R = \sum_{j=1}^3 \frac{n_j^0}{v_j} (-\Delta_{Rj} H_T)$$

sau :

$$(18') \quad \Delta H_R = n_{g.p.}^0 [X_{\text{CH}_4}^0 (-\Delta_{R_1} H_T) + X_{\text{H}_2}^0 (-\Delta_{R_2} H_T) + X_{\text{NH}_3}^0 (-\Delta_{R_3} H_T)],$$

În tabelul 5 sînt prezentate mărimile termodinamice necesare concretizării ecuațiilor (10), (14) și (18).

Tabelul 5

Mărimi termodinamice [5]

Com- ponent	H_f cal/mol	$C_{ps} = a_i + b_i T + c_i T^2$ cal/mol
CH ₄	-17 889,0	$3,422 + 17,845 \cdot 10^{-3} T - 4,165 \cdot 10^{-6} T^2$
H ₂	0,0	$6,88 + 0,066 \cdot 10^{-3} T + 0,279 \cdot 10^{-6} T^2$
NH ₃	-11 000,0	$8,04 + 0,7 \cdot 10^{-3} T + 5,1 \cdot 10^{-6} T^2$
N ₂	0,0	$6,30 + 1,8191 \cdot 10^{-3} T - 0,345 \cdot 10^{-6} T^2$
Ar	0,0	4,9675
O ₂	0,0	$6,13 + 2,99 \cdot 10^{-3} T - 0,806 \cdot 10^{-6} T^2$
CO ₂	-94 051,8	$6,85 + 8,533 \cdot 10^{-3} T - 2,475 \cdot 10^{-6} T^2$
H ₂ O	-57 797,9	$6,89 + 3,283 \cdot 10^{-3} T - 0,343 \cdot 10^{-6} T^2$

Ecuațiile efectelor termice ale reacțiilor (2) și (3), obținute prin integrarea relației lui Kirchhoff, pe baza datelor din tabelul 5, sînt de forma:

$$(19) \quad \Delta_R H_T = -192\,868,7284 + 4,948 T - 4,363 \cdot 10^{-3} T^2 + 0,872 \cdot 10^{-6} T^3,$$

$$(20) \quad \Delta_R H_T = -61\,062,5184 + 10,705 T + 0,861 \cdot 10^{-3} T^2 - 0,073 \cdot 10^{-6} T^3,$$

$$(21) \quad \Delta_R H_T = -76\,032,079 + 0,847 T + 1,4457 \cdot 10^{-3} T^2 - 1,7275 \cdot 10^{-6} T^3.$$

Înlocuind ecuațiile (19)...(21) în relația (18') se obține forma concretă a funcției (22):

$$(22) \quad \Delta H_R = n_{g.p.}^0 F(X_{CH_4}^0, X_{H_2}^0, X_{NH_3}^0, T) = n_{g.p.}^0 Y,$$

unde:

$$(23) \quad Y = A_0'' + B_0'' T + C_0'' T^2 + D_0'' T^3,$$

în care:

$$(24) \quad \begin{cases} A_0'' = 192\,868,7284 X_{CH_4}^0 + 61\,062,5184 X_{H_2}^0 + 76\,032,079 X_{NH_3}^0, \\ B_0'' = -4,948 X_{CH_4}^0 - 10,705 X_{H_2}^0 - 0,8475 X_{NH_3}^0, \\ C_0'' = (4,363 X_{CH_4}^0 - 0,861 X_{H_2}^0 - 1,44577 X_{NH_3}^0) \cdot 10^{-3}, \\ D_0'' = (-0,872 X_{CH_4}^0 + 0,073 X_{H_2}^0 + 1,7275 X_{NH_3}^0) \cdot 10^{-6}. \end{cases}$$

Consumul de combustibil, $n_{g.p.}^0$, se poate determina, în final, cu relația:

$$(25) \quad n_{g.p.}^0 = \frac{\Delta H_{ex}}{X + Y - Z}.$$

Cantitatea de căldură consumată în procesul de reformare catalitică, ΔH_{ex} , se determină cu relația:

$$\begin{aligned}
 \frac{\Delta H_{ex}}{(n_{CH_4}^0)_{tehn.}} = & 41\,100\alpha - 10\,320\beta + (32,50\alpha + 0,522\beta + 3,422 + \\
 & + 7,219\dot{X}_{H_2O}^0)T_p - (19,93\alpha - 4,134\beta - 8,922 - 1,187\dot{X}_{H_2O}^0) \cdot 10^{-3}T_p^2 + \\
 (26) \quad & + (2,85\alpha - 1,336\beta - 1,388 + 0,089\dot{X}_{H_2O}^0) \cdot 10^{-6}T_p^3 - \\
 & - (3,422 + 7,219\dot{X}_{H_2O}^0)T_{p0} - (8,922 - 1,187\dot{X}_{H_2O}^0) \cdot 10^{-3}T_{p0}^2 + \\
 & + (1,388 - 0,089\dot{X}_{H_2O}^0) \cdot 10^{-6}T_{p0}^3,
 \end{aligned}$$

stabilită anterior [6].

Gradele de transformare α , β se pot determina cu ajutorul modelului matematic al desfășurării procesului la echilibru [6] constituit din ecuațiile algebrice neliniare:

$$(27) \quad K_{p1}(1-\alpha)(\dot{X}_{H_2O}^0 - \alpha - \beta)(1 + \dot{X}_{H_2O}^0 + 2\alpha)^2 = (\alpha - \beta)(3\alpha + \beta)^3 p^2,$$

$$(28) \quad K_{p2}(\alpha - \beta)(\dot{X}_{H_2O}^0 - \alpha - \beta) = \beta(3\alpha + \beta),$$

$$\begin{aligned}
 (29) \quad \lg K_{p1} = & -\frac{9\,861,111}{T_p} - 11,87 - 2,058457 \cdot 10^{-3}T_p + \\
 & + 0,17795 \cdot 10^{-6}T_p^2 + 8,3432 \lg T_p,
 \end{aligned}$$

$$\begin{aligned}
 (30) \quad \lg K_{p2} = & \frac{2\,217,18}{T_p} - 3,274672 + 0,352381 \cdot 10^{-3}T_p - \\
 & - 0,05077 \cdot 10^{-6}T_p^2 + 0,2969 \lg T_p.
 \end{aligned}$$

Ecuațiile (12), (13), (16), (17), (23)...(30) permit calculul consumului de gaz combustibil ca funcție de parametrii procesului de reformare catalitică (P , T_p , T_{p0} , $\dot{X}_{H_2O}^0$), precum și de parametrii procesului de ardere (T_{01} , T_{02} , T , $X_{CH_4}^0$, $X_{H_2}^0$, $X_{NH_3}^0$, $X_{N_2}^0$ și φ):

$$(31) \quad \frac{n_{s.p.}^0}{(n_{CH_4}^0)_{tehn.}} = F(P, T_p, T_{p0}, \dot{X}_{H_2O}^0, T_{01}, T_{02}, T, X_{CH_4}^0, X_{H_2}^0, X_{NH_3}^0, X_{N_2}^0, \varphi).$$

Analiza, cu ajutorul calculatorului numeric, a sistemului de ecuații (12), (13), (16), (17) și (23)...(30), scris sub forma (31), permite determinarea consumului de combustibil la diferite valori ale parametrilor tehnologici precum și optimizarea acestora. Aceste ecuații au o formă generală putînd fi aplicate și pentru amestecuri formate din gaze de purjă – gaz metan cit și numai pentru gaz metan. În ultimul caz, înlocuind $X_{CH_4}^0 = 1$, $X_{NH_3}^0 = X_{H_2}^0 = X_{N_2}^0 = 0$ în ecuațiile (12), (13), (16), (17) și (23), (24), acestea capătă forma simplă stabilită anterior pentru cazul arderii gazului metan [1]:

$$(18') \quad X = 3,422 T_{01} + 8,9225 \cdot 10^{-3} T_{01}^2 - 1,3883 \cdot 10^{-6} T_{01}^3 - \\ - 1,77532 \cdot 10^3 + 9,5238 \varphi (6,2643 T_{02} + 1,03249 \cdot 10^{-3} T_{02}^2 - \\ - 0,14727 \cdot 10^{-6} T_{02}^3 - 1954,55),$$

$$(23') \quad Y = 192\,868,7284 - 4,948 T + 4,363 \cdot 10^{-3} T^2 - 0,872 \cdot 10^{-6} T^3, \\ Z = 8,37 T + 4,5595 \cdot 10^{-3} T^2 - 0,51633 \cdot 10^{-6} T^3 - 2\,885,4978 +$$

$$(17') \quad + 9,5238 \varphi (6,2643 T + 1,03249 \cdot 10^{-3} T^2 - \\ - 0,14725 \cdot 10^{-6} T^3 - 1\,954,5537).$$

4. Rezultate experimentale

Posibilitatea utilizării în practică a gazelor de purjă la ardere în amestec cu gaz metan s-a cercetat experimental pe reactorul industrial de reformare de la C. C. Slobozia. În acest scop s-a studiat influența compoziției și debitului de gaze de purjă asupra temperaturii gazelor de ardere la ieșirea din zona de radiație. Rezultatele sînt prezentate în tabelul 6.

Datele s-au obținut pentru: $(n_{\text{CH}_4}^0)_{\text{tehnol}} = 1\,026,78 \text{ kmol/h}$, $T_p = 1\,050^\circ\text{K}$, $\dot{X}_{\text{H}_2\text{O}}^0 = 4$, $P = 30 \text{ at}$, $T_{01} = 300^\circ\text{K}$, $T_{02} = 500^\circ\text{K}$, $\varphi = 1,12$ și debitul de gaz metan de combustie, de 300 kmol/h . Rezultatele obținute dovedesc că înlocuirea metanului cu o cantitate echivalentă de gaze de purjă duce la modificări nesemnificative ale temperaturii în focar.

Tabelul 6

Influența compoziției și debitului gazelor de purjă asupra temperaturii din focar

Debit g.p. $\text{m}^3 \text{ N/h}$	Compoziția, [% vol.]					T $^\circ\text{K}$
	NH_3	CH_4	H_2	N_2	Ar	
250	0,80	11,30	63,51	20,65	3,74	1 183
625	0,67	15,43	54,63	24,70	4,57	1 203
750	0,68	13,20	57,21	24,60	4,30	1 213
875	0,64	10,50	61,16	24,00	3,70	1 213
1 175	0,80	15,25	56,50	23,00	4,35	1 183
1 250	0,50 ₄	12,00	56,00	20,25	3,74	1 183
1 000	0,24	16,75	59,18	19,65	4,18	1 183
1 375	0,50	12,00	56,05	20,65	3,74	1 193
1 500	0,94	11,80	60,54	22,25	4,05	1 103
1 750	0,64	12,80	58,36	24,20	4,00	1 213

Rezultatele experimentale au fost confirmate de calculele efectuate cu ajutorul ecuațiilor stabilite în această lucrare. Rezolvarea ecuațiilor pentru stabilirea cantității de gaze combustibile $(n_{\text{g.p.}}^0)$, la diferite valori

ale parametrilor tehnologici: $P, T_p, T_{p0}, \dot{X}_{H_2O}^0, n_{CH_4}^0, \varphi, T_{01}, T_{02}, T, X_{NH_3}^0, X_{CH_4}^0, X_{H_2}^0, X_{N_2}^0$, s-a efectuat prin programare la un calculator digital. O parte din rezultatele obținute se dau sub forma tabelelor 7 și 8. Din aceste tabele rezultă influența principalilor parametri precum și echivalența calorică a gazelor de purjă exprimată prin gaz metan.

Tabelul 7

Variația consumului de gaz metan combustibil (kmol/kmol CH_4 tehnologic) cu T și φ la $T_p = 1100^\circ K, T_{p0} = 720^\circ K, P = 40$ at, $\dot{X}_{H_2O}^0 = 4$ ($\Delta H_{ex} = 66\,630$ kcal/kmol CH_4), iar $T_{01} = 300^\circ K, T_{02} = 500^\circ K$

$T, [^\circ K],$ φ	1 150	1 200	1 250	1 300
1,0	0,5036	0,5218	0,5415	0,5629
1,1	0,5223	0,5436	0,5669	0,5924
1,2	0,5425	0,5673	0,5948	0,6252
1,3	0,5643	0,5932	0,6255	0,6618

Tabelul 8

Variația consumului de gaz de purjă ($n_{g.p.}^0$) și echivalența acestuia în metan (EC) în condițiile $T_p = 1100^\circ K, T_{p0} = 720^\circ K, P = 40$ at, $\dot{X}_{H_2O}^0 = 4$ ($\Delta H_{ex} = 66\,630$ kcal/kmol CH_4), $T_{01} = 300^\circ K, T_{02} = 500^\circ K$ iar $X_{CH_4}^0 = 0,22, X_{H_2}^0 = 0,50, X_{NH_3}^0 = 0,077, X_{N_2}^0 = 0,213$

$T, [^\circ K],$ φ		1 150	1 200	1 250	1 300
1,0	$n_{g.p.}^0$	2,0105	2,1480	2,2950	2,4649
	EC	4,0101	4,1165	4,2383	4,3790
1,1	$n_{g.p.}^0$	2,1465	2,3006	2,4798	2,6906
	EC	4,1097	4,2321	4,3743	4,5424
1,2	$n_{g.p.}^0$	2,3931	2,6014	2,8513	3,1566
	EC	4,4113	4,5856	4,7777	5,0489
1,3	$n_{g.p.}^0$	2,6046	2,8690	3,1955	3,6090
	EC	4,6157	4,8365	5,1087	5,4533

5. Concluzii

1. S-a stabilit un model matematic de bilanț pentru determinarea consumului de gaz de purjă drept combustibil în cuptorul de reformare a metanului. Acest model este general, putînd fi aplicat și în cazul utilizării amestecurilor metan—gaze purjă sau numai metan.

2. S-a verificat experimental posibilitatea practică a înlocuirii parțiale a metanului cu gaze de purjă la ardere studiind influența compoziției amestecului metan—gaze purjă asupra temperaturii în focar.

3. Ecuatiile stabilite pentru calculul consumului de combustibil s-au programat la calculator în scopul analizei influenței globale a parametrilor tehnologici asupra consumurilor de gaz combustibil și a determinării echivalenței calorice a gazelor de purjă în diferite condiții.

Notații și indici

A_0, B_0, C_0, D_0	— constante definite de relațiile (13),
A'_0, B'_0, C'_0, D'_0	— constante definite de relațiile (17),
$A''_0, B''_0, C''_0, D''_0$	— constante definite de relațiile (24),
C_{pi}	— căldura specifică a componentului i ,
H_f	— căldura de formare a componentului i ,
ΔH_0	— entalpia fazelor gazoase la intrarea în cuptor,
ΔH	— entalpia gazelor de ardere la ieșirea din zona de radiație a cuptorului,
ΔH_R	— entalpia produsă în relațiile (2)...(4),
ΔH_{ex}	— entalpia cedată de către gazele de ardere procesului de reformare din tuburi,
$\Delta R_1 H_T, \Delta R_2 H_T, \Delta R_3 H_T$	— efectele termice ale reacțiilor (2), (3) și (4) la o temperatură oarecare,
K_{p1}, K_{p2}	— constantele de echilibru ale reacțiilor de reformare,
$n_{g.p.}^0$	— consumul de gaz combustibil, [kmol/h],
$(n_{CH_4}^0)_{tehn.}$	— consumul de gaz metan tehnologic, [kmol/h],
n_i	— debit molar de component i ,
P	— presiunea în reformer,
T_p, T_{p0}	— temperatura finală și inițială în procesul de reformare,
T_{01}, T_{02}	— temperatura inițială a gazului combustibil și respectiv a aerului,
T	— temperatura finală a gazelor de ardere,
X, Y, Z	— funcții definite prin relațiile (12), (16) și (23),
X_i^0	— fracția molară inițială a componentului i ,
X_{aer}^0	— raportul molar inițial $n_{aer}^0/n_{g.p.}^0$,
α, β	— grade de transformare în procesul de reformare,
$\varphi = \dot{X}_{aer}^0 / (\dot{X}_{aer}^0)_{stoichiometric}$	— coeficientul de exces de aer față de raportul stoichiometric

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THE EFFICIENCY OF PURGE GAS BURNING IN THE AMMONIA PLANTS

(Summary)

The natural gas is employed in ammonia plants not only as a raw material but also as a burning gas. A fraction of this natural burning gas can be saved by the combustion of the purge gas resulting from ammonia synthesis loop. A mathematical model allowing the computation of this fraction is established. The validity of the model is proved by comparing the plant scale measurement data with the solutions of the model in the same technological circumstances.

STABILIREA CONSUMURILOR SPECIFICE DE COCS ÎN PROCESUL DE DESCOMPUNERE A CALCARULUI ȘI DOLOMITEI

DE

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1. Introducere

Procesul chimic de descompunere termică a calcarului și dolomitei prezintă importanță pentru numeroase procese industriale din industria chimică anorganică, industria metalurgică, industria materialelor de construcții [1]...[8], [22]. Prin realizarea acestui proces, în domeniile menționate, se urmărește obținerea unui var sau a unui var dolomitic de calitate determinată și în același timp obținerea unei anumite compoziții a fazei gazoase [1], [2], [17]...[19].

În majoritatea proceselor industriale actuale descompunerea termică se realizează în cuptoare verticale cu cocs, utilizându-se diferite sorturi de materii prime, plecând de la calcare de calitate superioară până la diverse sorturi de dolomită [1], [8], [17].

Diversitatea materiilor prime impune un consum de cocs diferit pentru fiecare materie primă și determină obținerea calității stabilite a produselor în condiții tehnologice diferite.

În același timp, în instalațiile tehnologice actuale nu există posibilitatea măsurării directe a produselor primare, var și gaze.

Având în vedere aceste condiții, în cele ce urmează se prezintă o descriere cantitativă amănunțită a procesului de descompunere termică, prin utilizarea modelului matematic de bilanț, recurgând la o metodă de rezolvare a modelului matematic cu ajutorul calculatorului numeric.

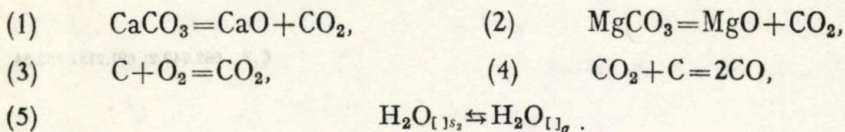
Modelul matematic și metoda de rezolvare a acestuia sînt astfel elaborate încît să poată fi utilizate pentru întreaga gamă de calcare și dolomite folosite în procesele industriale menționate.

2. Stabilirea modelului matematic de bilanț de masă și termic

Procesul de descompunere a materiilor prime carbonatice face parte din procesul industrial tip adsorbție—reacție—formare și creștere de germeni [1]. În condițiile realizării industriale a procesului, utilizînd cuptoarele verticale cu cocs și circulația în contracurent a fazelor reactant, ecuația caracteristică a procesului are forma :

$$\begin{aligned}
 & [\text{CaCO}_3 + \text{MgCO}_3 + \text{A}_1'']_{s_1} + [\text{C} + \text{H}_2\text{O} + \text{A}_2'']_{s_2} + [\text{O}_2 + \text{N}_2 + \text{H}_2\text{O}]_g = \\
 & = \{ [\text{CaCO}_3 + \text{MgCO}_3 + \text{A}_1'']_{s_1} + [\text{C} + \text{A}_2'']_{s_2} + [\text{CaO} + \text{MgO} + \text{A}_1'']_{s_3} \}_s + \\
 & \quad + [\text{CO} + \text{CO}_2 + \text{O}_2 + \text{N}_2 + \text{H}_2\text{O}]_g
 \end{aligned}$$

Această ecuație caracteristică implică următoarele procese elementare de transformare, independente :



După cum rezultă din ecuația caracteristică a procesului, în descrierea cantitativă s-a luat în considerare arderea incompletă a carbonului, fapt ce reflectă existența monoxidului de carbon în faza gazoasă finală.

În continuare, ca măsură a evoluției procesului, s-au definit gradele de transformare precum și relațiile de concretizare.

Gradele de transformare sînt definite prin relațiile :

$$(6) \quad \eta_{\text{CaCO}_3} = \frac{m_{\text{CaCO}_3}^0 - m_{\text{CaCO}_3}}{m_{\text{CaCO}_3}^0} = \frac{m_{\text{CaO}}}{\frac{M_{\text{CaO}}}{M_{\text{CaCO}_3}} m_{\text{CaCO}_3}^0} = \frac{m_{\text{CO}_2}^1 - m_{\text{CO}_2}^0}{\frac{M_{\text{CO}_2}}{M_{\text{CaCO}_3}} m_{\text{CaCO}_3}^0},$$

$$(7) \quad \eta_{\text{MgCO}_3} = \frac{m_{\text{MgCO}_3}^0 - m_{\text{MgCO}_3}}{m_{\text{MgCO}_3}^0} = \frac{m_{\text{MgO}}}{\frac{M_{\text{MgO}}}{M_{\text{MgCO}_3}} m_{\text{MgCO}_3}^0} = \frac{m_{\text{CO}_2}^2 - m_{\text{CO}_2}^0}{\frac{M_{\text{CO}_2}}{M_{\text{MgCO}_3}} m_{\text{MgCO}_3}^0},$$

$$(8) \quad \eta_{\text{O}_2} = \frac{m_{\text{O}_2}^0 - m_{\text{O}_2}}{m_{\text{O}_2}^0} = \frac{m_{\text{C}}^0 - m_{\text{C}}^3}{\frac{M_{\text{C}}}{M_{\text{O}_2}} m_{\text{O}_2}^0} = \frac{m_{\text{CO}_2}^3}{\frac{M_{\text{CO}_2}}{M_{\text{O}_2}} m_{\text{O}_2}^0},$$

$$(9) \quad \eta_{\text{C}} = \frac{m_{\text{C}}^0 - m_{\text{C}}}{m_{\text{C}}^0} = \frac{m_{\text{CO}_2}^0 - m_{\text{CO}_2}}{m_{\text{C}}^0} = \frac{m_{\text{CO}}}{2 \frac{M_{\text{CO}}}{M_{\text{C}}} m_{\text{C}}^0},$$

$$(10) \quad \eta_{\text{H}_2\text{O}_{(l)L}} = \frac{m_{\text{H}_2\text{O}_{(l)s_2}}^0 - m_{\text{H}_2\text{O}_{(l)s_2}}}{m_{\text{H}_2\text{O}_{(l)s_2}}^0} = \frac{m_{\text{H}_2\text{O}_{(l)g}} - m_{\text{H}_2\text{O}_{(l)g}}^0}{m_{\text{H}_2\text{O}_{(l)s_2}}^0}.$$

Relațiile de concretizare au forma :

$$(11) \quad m_{\text{CO}_2}^0 = m_{\text{CO}_2}^1 + m_{\text{CO}_2}^2, \quad (12) \quad m_{\text{CO}_2}^3 = m_{\text{CO}_2}^0 + m_{\text{CO}_2}^2,$$

$$(13) \quad m_{\text{C}}^0 = m_{\text{C}}^3, \quad (14) \quad \eta_{\text{H}_2\text{O}_{(l)L}} = 1.$$

Utilizînd relațiile de definiție a gradelor de transformare (6)...(10) precum și relațiile de concretizare (11)...(14) s-au elaborat ecuațiile algebrice de bilanț primare, prezentate în tabelele 1 și 2.

Tabelul 1

Ecuații algebrice de bilanț de masă primare în unități masice

Secția II

Faza	Compo- nentul	Inițial		Faza	Compo- nentul	La un moment dat	
		m	$\bar{X}$			m	
Solidă I $\square_{s_1}$	CaCO ₃	$m_{CaCO_3 \Pi_{s_1}}^0$	$\bar{X}_{CaCO_3 \Pi_{s_1}}^0$	Solidă $\square_s$	CaCO ₃	$m_{CaCO_3 \Pi_s}^0$	$\bar{X}_{CaCO_3 \Pi_s}^0 (1 - \eta_{CaCO_3})$
	MgCO ₃	$m_{MgCO_3 \Pi_{s_1}}^0$	$\bar{X}_{MgCO_3 \Pi_{s_1}}^0$		MgCO ₃	$m_{MgCO_3 \Pi_s}^0$	$\bar{X}_{MgCO_3 \Pi_s}^0 (1 - \eta_{MgCO_3})$
	A''	$m_{A'' \Pi_{s_1}}^0$	$\bar{X}_{A'' \Pi_{s_1}}^0$		CaO	$m_{CaO \Pi_s}^0$	$\frac{M_{CaO}}{M_{CaCO_3}} m_{CaCO_3 \Pi_s}^0 \bar{X}_{CaCO_3 \Pi_s}^0 \eta_{CaCO_3}$
	Total	$m_{\Pi_{s_1}}^0$	1		MgO	$m_{MgO \Pi_s}^0$	$\frac{M_{MgO}}{M_{MgCO_3}} m_{MgCO_3 \Pi_s}^0 \bar{X}_{MgCO_3 \Pi_s}^0 \eta_{MgCO_3}$
	C	$m_{C \Pi_{s_1}}^0$	$\bar{X}_{C \Pi_{s_1}}^0$		C	$m_{C \Pi_s}^0$	$\frac{M_C}{M_{O_2}} \bar{X}_{C \Pi_s}^0 (1 - \eta_C) - \frac{M_C}{M_{O_2}} m_{O_2 \Pi_s}^0 \bar{X}_{O_2 \Pi_s}^0 \eta_{O_2} (1 - \eta_C)$
Solidă $\square_{s_2}$	H ₂ O	$m_{H_2O \Pi_{s_2}}^0$	$\bar{X}_{H_2O \Pi_{s_2}}^0$	Gazoasă $\square_g$	A''	$m_{A'' \Pi_s}^0$	$m_{A'' \Pi_s}^0 \bar{X}_{A'' \Pi_s}^0 + m_{\Pi_{s_2}}^0 \bar{X}_{A'' \Pi_{s_2}}^0$
	A''	$m_{A'' \Pi_{s_2}}^0$	$\bar{X}_{A'' \Pi_{s_2}}^0$		Total	$m_{\Pi_s}^0$	$m_{\Pi_s}^0 \left(1 - \frac{M_{CO_2}}{M_{CaCO_3}} \bar{X}_{CaCO_3 \Pi_{s_1}}^0 \eta_{CaCO_3} - \frac{M_{CO_2}}{M_{MgCO_3}} \bar{X}_{MgCO_3 \Pi_{s_1}}^0 \eta_{MgCO_3} \right) + m_{\Pi_{s_2}}^0 [(1 - \bar{X}_{C \Pi_{s_2}}^0 \eta_C) - \bar{X}_{H_2O \Pi_{s_2}}^0 \eta_{O_2} (1 - \eta_C)]$
	Total	$m_{\Pi_{s_2}}^0$	1		CO	$m_{CO \Pi_g}^0$	$\frac{M_{CO}}{M_C} \left(m_{\Pi_{s_2}}^0 \bar{X}_{CO \Pi_{s_2}}^0 - \frac{M_C}{M_{O_2}} m_{\Pi_g}^0 \bar{X}_{O_2 \Pi_g}^0 \eta_{O_2} \right) \eta_C$
	O ₂	$m_{O_2 \Pi_g}^0$	$\bar{X}_{O_2 \Pi_g}^0$		CO ₂	$m_{CO_2 \Pi_g}^0$	$M_{CO_2} m_{\Pi_{s_1}}^0 \left(\frac{\bar{X}_{CaCO_3 \Pi_{s_1}}^0}{M_{CaCO_3}} \eta_{CaCO_3} + \frac{\bar{X}_{MgCO_3 \Pi_{s_1}}^0}{M_{MgCO_3}} \eta_{MgCO_3} \right) + m_{\Pi_g}^0 \bar{X}_{O_2 \Pi_g}^0 \frac{M_{CO_2}}{M_{O_2}} \eta_{O_2} - \frac{M_{CO_2}}{M_C} m_{\Pi_{s_2}}^0 \bar{X}_{CO \Pi_{s_2}}^0 \eta_C$
	N ₂	$m_{N_2 \Pi_g}^0$	$\bar{X}_{N_2 \Pi_g}^0$		O ₂	$m_{O_2 \Pi_g}^0$	$m_{O_2 \Pi_g}^0 \bar{X}_{O_2 \Pi_g}^0 (1 - \eta_{O_2})$
Gazoasă $\square_g$	H ₂ O	$m_{H_2O \Pi_g}^0$	$\bar{X}_{H_2O \Pi_g}^0$	Total	N ₂	$m_{N_2 \Pi_g}^0$	$m_{N_2 \Pi_g}^0 \bar{X}_{N_2 \Pi_g}^0$
	Total	$m_{\Pi_g}^0$	1		H ₂ O	$m_{H_2O \Pi_g}^0$	$m_{H_2O \Pi_g}^0 \bar{X}_{H_2O \Pi_g}^0 + m_{\Pi_{s_2}}^0 \bar{X}_{H_2O \Pi_{s_2}}^0$
					Total	$m_{\Pi_g}^0$	$m_{\Pi_g}^0 \left(1 + \frac{M_C}{M_{O_2}} \bar{X}_{O_2 \Pi_g}^0 \eta_{O_2} \right) + m_{\Pi_{s_2}}^0 \bar{X}_{H_2O \Pi_{s_2}}^0 + \left[m_{\Pi_{s_2}}^0 \bar{X}_{CO \Pi_{s_2}}^0 - \frac{M_C}{M_{O_2}} m_{\Pi_g}^0 \bar{X}_{O_2 \Pi_g}^0 \eta_{O_2} \right] \eta_C + M_{CO_2} m_{\Pi_{s_1}}^0 \left[\frac{\bar{X}_{CaCO_3 \Pi_{s_1}}^0}{M_{CaCO_3}} \eta_{CaCO_3} + \frac{\bar{X}_{MgCO_3 \Pi_{s_1}}^0}{M_{MgCO_3}} \eta_{MgCO_3} \right]$

Ecuatii algebrice de bilanț primare în unități masice pentru solid și volume pentru gaz

Faza	Com- ponentul	Initial		Faza	Comp. ponentul	Final
		$m(V)$	$\bar{X}$			$m(V)$
Solidă 1 [] _{s1}	CaCO ₃	$m_{CaCO_3[]_{s1}}^0$	$\bar{X}_{CaCO_3[]_{s1}}^0$	CaCO ₃	$m_{CaCO_3[]_s} = m_{[]_{s1}}^0 \bar{X}_{CaCO_3[]_{s1}}^0 (1 - \eta_{CaCO_3})$	
	MgCO ₃	$m_{MgCO_3[]_{s1}}^0$	$\bar{X}_{MgCO_3[]_{s1}}^0$	MgCO ₃	$m_{MgCO_3[]_s} = m_{[]_{s1}}^0 \bar{X}_{MgCO_3[]_{s1}}^0 (1 - \eta_{MgCO_3})$	
	A''	$m_{A''[]_{s1}}^0$	$\bar{X}_{A''[]_{s1}}^0$	CaO	$m_{CaO[]_s} = 0,56 m_{[]_{s1}}^0 \bar{X}_{CaCO_3[]_{s1}}^0 \eta_{CaCO_3}$	
	Total	$m_{[]_{s1}}^0$	1	MgO	$m_{MgO[]_s} = 0,47169 m_{[]_{s1}}^0 \bar{X}_{MgCO_3[]_{s1}}^0 \eta_{MgCO_3}$	
	C	$m_{C[]_{s1}}^0$	$\bar{X}_{C[]_{s1}}^0$	C	$m_{C[]_s} = m_{[]_{s1}}^0 \bar{X}_{C[]_{s1}}^0 (1 - \alpha \eta_O) (1 - \eta_C)$	
Solidă 2 [] _{s2}	H ₂ O	$m_{H_2O[]_{s2}}^0$	$\bar{X}_{H_2O[]_{s2}}^0$	A''	$m_{A''[]_s} = m_{[]_{s1}}^0 (1 - \bar{X}_{CaCO_3[]_{s1}}^0 - \bar{X}_{MgCO_3[]_{s1}}^0) + m_{[]_{s2}}^0 (1 - \bar{X}_{C[]_{s2}}^0 - \bar{X}_{H_2O[]_{s2}}^0)$	
	A''	$m_{A''[]_{s2}}^0$	$\bar{X}_{A''[]_{s2}}^0$	Total	$m_{[]_s} = m_{[]_{s1}}^0 (1 - 0,44 \bar{X}_{CaCO_3[]_{s1}}^0 \eta_{CaCO_3} - 0,52381 \bar{X}_{MgCO_3[]_{s1}}^0 \eta_{MgCO_3}) + m_{[]_{s2}}^0 \{1 - \bar{X}_{H_2O[]_{s2}}^0 - \bar{X}_{C[]_{s2}}^0 [1 - (1 - \alpha \eta_O) (1 - \eta_C)]\}$	
	Total	$m_{[]_{s2}}^0$	1	CO	$V_{CO[]_g} = 3,735 m_{[]_{s2}}^0 \bar{X}_{C[]_{s2}}^0 (1 - \alpha \eta_O) \eta_C$	
	O ₂	$V_{O_2[]_g}^0 = 1,8675 m_{[]_{s2}}^0 \bar{X}_{C[]_{s2}}^0 \alpha$		CO ₂	$V_{CO_2[]_{s1}} = m_{[]_{s1}}^0 (0,2241 \bar{X}_{CaCO_3[]_{s1}}^0 \eta_{CaCO_3} + 0,26678 \bar{X}_{MgCO_3[]_{s1}}^0 \eta_{MgCO_3}) + 1,8675 \bar{X}_{C[]_{s2}}^0 [\eta_{O_2} - (1 - \alpha \eta_O) \eta_C]$	
	N ₂	$V_{N_2[]_g}^0 = 1,8675 m_{[]_{s2}}^0 \bar{X}_{C[]_{s2}}^0 \frac{\alpha}{X_{O_2[]_{s2}}^0} \frac{X_{N_2[]_g}^0}{X_{O_2[]_g}^0}$		O ₂	$V_{O_2[]_g} = 1,8675 m_{[]_{s2}}^0 \bar{X}_{C[]_{s2}}^0 \alpha (1 - \eta_{O_2})$	
Gazoasă [] _g	H ₂ O	$V_{H_2O[]_g}^0 = 1,8675 m_{[]_{s2}}^0 \bar{X}_{C[]_{s2}}^0 \frac{\alpha}{X_{O_2[]_{s2}}^0} \frac{X_{H_2O[]_g}^0}{X_{O_2[]_g}^0}$		N ₂	$V_{N_2[]_g} = 1,8675 m_{[]_{s2}}^0 \bar{X}_{C[]_{s2}}^0 \frac{\alpha}{X_{O_2[]_{s2}}^0} \frac{X_{N_2[]_g}^0}{X_{O_2[]_g}^0}$	
	Total	$V_{[]_g}^0 = 1,8675 m_{[]_{s2}}^0 \bar{X}_{C[]_{s2}}^0 \frac{\alpha}{X_{O_2[]_{s2}}^0} \frac{X_{H_2O[]_g}^0}{X_{O_2[]_g}^0} + 1,5 \alpha \bar{X}_{C[]_{s2}}^0 \frac{X_{H_2O[]_g}^0}{X_{O_2[]_g}^0}$		H ₂ O	$V_{H_2O[]_g} = 1,245 m_{[]_{s2}}^0 \left[\bar{X}_{H_2O[]_{s2}}^0 + 1,5 \alpha \bar{X}_{C[]_{s2}}^0 \frac{X_{H_2O[]_g}^0}{X_{O_2[]_g}^0} \right]$	
				Total	$V_{[]_g} = m_{[]_{s1}}^0 (0,2241 \bar{X}_{CaCO_3[]_{s1}}^0 \eta_{CaCO_3} + 0,26678 \bar{X}_{MgCO_3[]_{s1}}^0 \eta_{MgCO_3}) + 1,245 m_{H_2O[]_{s2}}^0 + 1,8675 m_{[]_{s2}}^0 \bar{X}_{C[]_{s2}}^0 \left\{ \alpha \left[\frac{1 - \bar{X}_{O_2[]_g}^0}{X_{O_2[]_g}^0} + 1 - \eta_{O_2} (1 + \eta_C) \right] + \eta_{O_2} + \eta_C \right\}$	

Tabelul 3

Faza	Compo- nentul	Inițial		Faza	Compo- nentul	Final	
		$m(V)$	$\bar{X}(X)$			$m(V)$	
Solidă 1 [] _{s1}	CaCO ₃	$m_{CaCO_3(l)s_1}^0$	$\bar{X}_{CaCO_3(l)s_1}^0$	Solidă [] _s	CaCO ₃	$m_{CaCO_3(l)s}^0 = m_{CaCO_3(l)s_1}^0 - \frac{M_{CaCO_3}}{M_{CaO}} m_{CaO(l)s}$	
	MgCO ₃	$m_{MgCO_3(l)s_1}^0$	$\bar{X}_{MgCO_3(l)s_1}^0$		MgCO ₃	$m_{MgCO_3(l)s}^0 = m_{MgCO_3(l)s_1}^0 - \frac{M_{MgCO_3}}{V_M} \left[V_{(l)s} \left(X_{CO_2(l)s} + X_{O_2(l)s} + \frac{1}{2} X_{CO(l)s} \right) - \frac{V_M}{M_{CaO}} m_{CaO(l)s} \bar{X}_{CaO(l)s} - V_{(l)s}^0 \bar{X}_{O_2(l)s} \right]$	
	A*	$m_{A^*(l)s_1}^0$	$\bar{X}_{A^*(l)s_1}^0$		CaO	$m_{CaO(l)s} = m_{(l)s}^0 - \bar{X}_{CaO(l)s}$	
	Total	$m_{(l)s_1}^0$	1		MgO	$m_{MgO(l)s} = \frac{M_{MgO}}{V_M} \left[V_{(l)s} \left(X_{CO_2(l)s} + X_{O_2(l)s} + \frac{1}{2} X_{CO(l)s} \right) - \frac{V_M}{M_{CaO}} m_{CaO(l)s} \bar{X}_{CaO(l)s} - V_{(l)s}^0 \bar{X}_{O_2(l)s} \right]$	
	C	$m_{C(l)s_2}^0$	$\bar{X}_{C(l)s_2}^0$		A*	$m_{A^*(l)s} = m_{(l)s_1}^0 - \bar{X}_{A^*(l)s_1}^0 \bar{X}_{A^*(l)s}$	
Solidă 2 [] _{s2}	H ₂ O	$m_{H_2O(l)s_2}^0$	$\bar{X}_{H_2O(l)s_2}^0$	Gazoasă [] _g	C	$m_{C(l)s} = m_{(l)s_2}^0 - \frac{M_C}{V_M} (V_{(l)s}^0 \bar{X}_{CO_2(l)s} - V_{(l)s} X_{O_2(l)s}) - V_{(l)s} X_{CO(l)s} \frac{1}{2} \frac{M_C}{V_M}$	
	A*	$m_{A^*(l)s_2}^0$	$\bar{X}_{A^*(l)s_2}^0$		Total	$m_{(l)s} = m_{(l)s_1}^0 + m_{(l)s_2}^0 (1 - \bar{X}_{H_2O(l)s_2}^0) + V_{(l)s}^0 \bar{X}_{O_2(l)s_2}^0 - \frac{M_{O_2}}{V_M} \frac{V_M}{V_{(l)s}^0} \frac{m_{(l)s_2}^0 \bar{X}_{H_2O(l)s_2}^0}{1 - X_{O_2(l)s_2}^0 - X_{CO_2(l)s_2}^0} M_{CO_2} X_{CO_2(l)s_2} + M_{O_2} X_{O_2(l)s_2} + \frac{1}{2} (M_C + M_{CO_2}) X_{CO(l)s_2} \frac{1}{V_M}$	
	Total	$m_{(l)g}^0$	1		O ₂	$V_{O_2(l)s} = V_{(l)s} X_{O_2(l)s}$	
	O ₂	$V_{O_2(l)g}^0$	$X_{O_2(l)g}^0$		N ₂	$V_{N_2(l)s} = V_{(l)s}^0 X_{N_2(l)s}^0$	
	N ₂	$V_{N_2(l)g}^0$	$X_{N_2(l)g}^0$		CO	$V_{CO(l)s} = V_{(l)s} X_{CO(l)s}$	
Gazoasă [] _g	H ₂ O	$V_{H_2O(l)g}^0$	$X_{H_2O(l)g}^0$	Gazoasă [] _g	CO ₂	$V_{CO_2(l)s} = V_{(l)s} X_{CO_2(l)s}$	
	Total	$V_{(l)g}^0$	1		H ₂ O	$V_{H_2O(l)g} = V_{(l)s}^0 X_{H_2O(l)s}^0 + \frac{V_M}{M_{H_2O}} m_{(l)s_2}^0 \bar{X}_{H_2O(l)s_2}^0$	
	O ₂				Total	$V_{(l)g} = \frac{V_{(l)s}^0 (1 - X_{O_2(l)s}^0) + \frac{V_M}{M_{H_2O}} m_{(l)s_2}^0 \bar{X}_{H_2O(l)s_2}^0}{1 - X_{O_2(l)s}^0 - X_{CO_2(l)s}^0 - X_{CO(l)s}^0}$	
	N ₂						
	H ₂ O						

Analizînd ecuațiile din tabelele 1 și 2 se constată că rezolvarea modelului matematic de bilanț de masă necesită determinarea a cinci mărimi și anume: α — coeficientul excesului de aer și cele patru grade de transformare. Obținerea acestor mărimi este dificilă, necesitînd măsurători pretențioase și de aceea s-au elaborat, pe baza ecuațiilor de transformare:

$$(15) \quad V_{[1]g}^0 X_{O_2[1]g}^0 \eta_{O_2} = V_{[1]g}^0 X_{O_2[1]g}^0 - V_{[1]g} X_{O_2[1]g},$$

$$(16) \quad (m_{[1]s}^0 \bar{X}_{CO[1]s}^0 - \frac{M_C}{V_M} V_{[1]g}^0 X_{O_2[1]g}^0 \eta_{O_2}) \eta_C = \frac{M_C}{2V_M} V_{[1]g} X_{CO[1]g},$$

$$(17) \quad m_{[1]s}^0 \bar{X}_{CaCO_3[1]s}^0 \eta_{CaCO_3} = \frac{M_{CaCO_3}}{M_{CaO}} m_{[1]s} \bar{X}_{CaO[1]s},$$

$$(18) \quad m_{[1]s}^0 \bar{X}_{MgCO_3[1]s}^0 \eta_{MgCO_3} = \frac{M_{MgCO_3}}{M_{MgO}} m_{[1]s} \bar{X}_{MgO[1]s},$$

sau:

$$(19) \quad m_{[1]s}^0 \bar{X}_{MgCO_3[1]s}^0 \eta_{MgCO_3} = \frac{M_{MgCO_3}}{V_M} \left[V_{[1]g} \left(\bar{X}_{O_2[1]g} + X_{CO_2[1]g} + \frac{1}{2} X_{CO[1]g} \right) - \frac{V_M}{M_{CaO}} m_{[1]s} \bar{X}_{CaO[1]s} - V_{[1]g}^0 X_{O_2[1]g}^0 \right],$$

ecuațiile de bilanț secundare [11], [20].

După cum se poate constata din ecuațiile de bilanț secundare, prezentate în tabelul 3, necunoscutele ce apar sînt de data aceasta acelea care pot fi obținute direct prin măsurătorile efectuate în mod curent în fiecare uzină. Deci rezolvarea numerică a modelului matematic de bilanț de masă necesită măsurarea directă a următoarelor patru mărimi: $X_{O_2[1]g}$, $X_{CO[1]g}$, $\bar{X}_{CaO[1]s}$, $\bar{X}_{MgO[1]s}$ sau $X_{CO_2[1]g}$. Sub această formă bilanțul se poate soluționa cunoscîndu-se masele reactanților, de calcar, de cocs și de aer.

Pentru a putea descrie complet procesul studiat, cu posibilitatea determinării mărimilor de mai sus, s-a trecut, în continuare, la elaborarea bilanțului termic.

Stabilirea sistemului ecuațiilor algebrice de bilanț termic s-a făcut utilizînd bilanțul global al reactorului, neținînd seama de specificitatea anumitor zone [2], [12]...[18]. În aceste condiții ecuația generală de bilanț are forma:

$$(20) \quad Q_{[1]s}^0 + Q_{[1]s_1}^0 + Q_{[1]g}^0 + \Delta_R H_T = Q_{[1]s} + Q_{[1]g} + \Delta_{R_D} H_T + Q_{vap} + Q_P$$

unde: $Q_{[1]s}^0$ — căldura fazei solide la intrarea în cuptor, $Q_{[1]s_1}^0$ — căldura cocsului la intrarea în cuptor, $Q_{[1]g}^0$ — căldura fazei gazoase la intrare în cuptor, $\Delta_R H_T$ — căldura degajată la arderea combustibilului, $Q_{[1]s}$ — căldura solidului la ieșirea din cuptor, Q_{vap} — căldura necesară vaporizării

Tabelul 4

Ecuațiile de bilanș termic

$Q_{\Pi_1}^0 = m_{\Pi_1}^0 \bar{c}_{\Pi_1}^0 t_{\Pi_1}$	
$Q_{\Pi_2}^0 = m_{\Pi_2}^0 [(1 - \bar{X}_{H_2O, \Pi_2}^0) \bar{C}_{p, \text{goc}} + \bar{X}_{H_2O, \Pi_2}^0 C_{p, H_2O}] t_{\Pi_2}^0$	
$Q_{\Pi_g}^0 = \frac{1}{V_M} 1,875 m_{\Pi_g}^0 \bar{X}_{Cu, s}^0 \alpha \frac{1}{X_{O, \Pi_g}^0} \int_{273}^{T_{\Pi_g}^0} C_p(T) dT$	
$\Delta_R H_T = \frac{1}{V_M} 1,8675 m_{Cu, s}^0 \alpha \eta_{O_2} \Delta_{R_3} H_T + \frac{1}{2 V_M} 3,735 m_{\Pi_3}^0 \bar{X}_{Cu, s}^0 (1 - \alpha \eta_{O_2}) \eta_{CO} \Delta_{R_4} H_T$	
$Q_{\Pi_3}^0 = m_{\Pi_3}^0 (1 - 0,44 \bar{X}_{CaCO_3, \Pi_3}^0 \eta_{CaCO_3} + 0,5238 \bar{X}_{MgCO_3, \Pi_3}^0 \eta_{MgCO_3}) \bar{C}_p t_{\Pi_3} + m_{\Pi_3}^0 \{1 - \bar{X}_{H_2O, \Pi_3}^0 - \bar{X}_{Cu, s}^0 [1 - (1 - \alpha \eta_{O_2})(1 - \eta_C)]\} \bar{C}_p t_{\Pi_3}$	
$Q_{\Pi_g}^0 = \frac{1,8675}{V_M} m_{\Pi_g}^0 \bar{X}_{Cu, s}^0 \left[\alpha \frac{X_{N_2, \Pi_g}^0}{X_{O_2, \Pi_g}^0} \int_{273}^{T_{\Pi_g}} C_{p, N_2}(T) dT + \alpha (1 - \eta_{O_2}) \int_{273}^{T_{\Pi_g}} C_{p, O_2}(T) dT + 2(1 - \alpha \eta_{O_2}) \eta_C \int_{273}^{T_{\Pi_g}} C_{p, CO}(T) dT + \right.$	
$\left. + \frac{1,245}{V_M} m_{\Pi_3}^0 \left(\bar{X}_{H_2O, \Pi_3}^0 + 1,5 \alpha \bar{X}_{Cu, s}^0 \frac{X_{H_2O, \Pi_g}^0}{X_{O_2, \Pi_g}^0} \right) \int_{273}^{T_{\Pi_g}} C_{p, H_2O}(T) dT + \frac{1,8675}{V_M} m_{\Pi_3}^0 \bar{X}_{Cu, s}^0 [\eta_{O_2} - (1 - \alpha \eta_{O_2}) \eta_C] \int_{273}^{T_{\Pi_g}} C_{p, CO_2}(T) dT + \right.$	
$\left. + \frac{1}{V_M} m_{\Pi_3}^0 (0,2241 \bar{X}_{CaCO_3, \Pi_3}^0 \eta_{CaCO_3} + 0,26678 \bar{X}_{MgCO_3, \Pi_3}^0 \eta_{MgCO_3}) \int_{273}^{T_{\Pi_g}} C_{p, CO_2}(T) dT \right.$	
$\Delta_R H_T = 0,01 m_{\Pi_3}^0 \bar{X}_{CaCO_3, \Pi_3}^0 \eta_{CaCO_3} \Delta_{R_1} H_T + 0,0119 m_{\Pi_3}^0 \bar{X}_{MgCO_3, \Pi_3}^0 \eta_{MgCO_3} \Delta_{R_2} H_T$	
$Q_{vap} = m_{\Pi_3}^0 \bar{X}_{H_2O, \Pi_3}^0 \Delta H_{vap}(T)$	
$Q_p = \sum A_i \Delta H_{pp_i}(T)$	

apei, $Q_{[g]}$ — căldura gazului la ieșire din cuptor, Q_p — căldura pierdută, $\Delta_{R,D}H_T$ — căldura consumată în procesul de descompunere.

Ecuatiile de bilanț, pe componenți, a ecuației (20), sînt prezentate în tabelul 4.

Tabelul 5
Mărimi termice

Nr. crt.	Faza	H_f^0 J/mol	C_p J/mol grad
1	CaCO ₃	s	-1 211 701
2	CaO	s	- 635 578
3	MgCO ₃	s	-1 121 713
4	MgO	s	- 611 501
5	O ₂	g	0
6	CO	g	- 110 562
7	CO ₂	g	- 395 653
8	C	s	- 10 882,3
9	N ₂	g	0
10	Aer	g	—
11	H ₂ O	g	—
12	Calcar	s	—
13	Cocs	s	—
14	Cenușă	s	—

Tabelul 6
Ecuatiile efectelor termice ale celor cinci procese elementare

$\Delta_R H_T^0 = j(T)$	[J/mol]
$\Delta_{R_1} H_T^0$	$186\,610 - 11,845\,T + 3,10351 \cdot 10^{-3} T^2 - 34,53 \cdot 10^{-7} T^3 - 8,35425 \cdot 10^5 / T$
$\Delta_{R_2} H_T^0$	$186\,610 - 18,79\,T + 3,10351 \cdot 10^{-3} T^2 - 34,53 \cdot 10^{-7} T^3 - 8,35425 \cdot 10^5 / T$
$\Delta_{R_3} H_T^0$	$119\,332 - 3,8329\,T - 8,5176 \cdot 10^{-3} T^2 - 34,53 \cdot 10^{-7} T^3 - 8,67647 \cdot 10^5 / T$
$\Delta_{R_4} H_T^0$	$-367\,227,43 + 59,6223\,T - 5,2 \cdot 10^{-3} T^2 + 98,3579 \cdot 10^{-7} T^3 - 2,878575 \cdot 10^{-9} T^4$
$\Delta_{R_5} H_T^0$	$90\,392 + 14,471425\,T - 19,2112 \cdot 10^{-3} T^2 + 8,383615 \cdot 10^{-7} T^3 - 1,439 \cdot 10^{-9} T^4$
$\Delta_{R_6} H_T^0$	$3091,5 - 2,1855\,T^*)$

*) kJ/kg.

După cum rezultă din sistemul ecuațiilor de bilanț de masă și termic, rezolvarea numerică necesită o serie de valori ce pot fi grupate astfel :

a) mărimi care caracterizează fazele reactant ; b) proprietăți termodinamice ale fazelor și componenților ; c) mărimi care caracterizează funcționarea instalației ($m_{[s_1]}^0, m_{[s_2]}^0, V_{[g]}^0, X_{CO_{[g]}}, X_{CO_{[s]}}, X_{O_{[g]}}, X_{CaO_{[s]}}, X_{MgO_{[s]}}, T_{[g]}, T_{[s]}, T_p$).

Mărimile din grupele a) și c) pot fi preluate din instalația industrială dar cele din grupa b) necesită un studiu teoretic.

Pentru determinarea proprietăților termice a fazelor și a componentelor din sistem s-a cercetat literatura de specialitate [1]...[10]. O primă constatare a fost aceea că datele termice, mai ales acelea referitoare la efectul termic în procesul de descompunere a calcarului, diferă foarte mult în cadrul acelorași condiții, de la autor la autor. Această constatare a impus necesitatea alegerii mărimilor numai după o verificare prealabilă a acestora. Drept criteriu de verificare s-a ales metoda de bilanț termic [20].

În urma analizei efectuate s-au calculat mărimile termice care pot fi luate în considerare în calcul, în limita erorilor de circa 5%. Aceste mărimi sînt prezentate în tabelele 5 și 6.

3. Rezolvarea numerică a modelului matematic de bilanț în vederea stabilirii consumurilor specifice de cocs

Modelul matematic de bilanț elaborat permite calculul consumului teoretic și real de cocs în funcție de natura materiilor prime (calcar, dolomită, cocs) și de condițiile de realizare practică a procesului. Totodată modelul permite determinarea ulterioară, prin calcul, a pierderilor de căldură și a randamentului termic al cuptorului. De asemenea, fiind dat raportul cocs/materie primă carbonatică și cunoscîndu-se parametrii procesului, modelul poate servi la determinarea debitelor fazelor care conțin produsele de reacție.

Avînd în vedere faptul că determinarea consumului specific de combustibil necesită un volum mare de calcul, s-a elaborat un program de rezolvare pe calculator a modelului propus.

Algoritmul de rezolvare are la bază metoda aproximărilor succesive. Drept criteriu de convergență s-a ales egalitatea descrisă de ecuația :

$$Q_{I,s}^0(m_{\text{cocs}}^0) + Q_{I,g}^0(m_{\text{cocs}}^0) + \Delta_R H_T(m_{\text{cocs}}^0) - Q_{I,g}(m_{\text{cocs}}^0) = Q_{I,s} - Q_{I,s}^0 + \Delta_R H_T + Q_{\text{vap}}.$$

Schema logică de rezolvare a modelului matematic de bilanț este prezentată în fig. 1.

Rezolvînd modelul matematic pentru o anumită calitate a materiilor prime (calcar, cocs) precum și pentru valorile medii ale gradelor de transformare obținute la realizarea industrială a procesului s-au obținut dependențele prezentate în fig. 2...4.

După cum se constată din analiza datelor prezentate în fig. 2...4 consumurile teoretice de cocs sînt mult influențate, pentru aceleași calități de calcar și cocs, de temperaturile fazelor produșilor de reacție și de temperatura de desfășurare a procesului.

Abaterile parametrilor fazelor produșilor de reacție de la valorile impuse de normele tehnologice pot duce la creșteri importante ale consumului de combustibil. Astfel o creștere cu 100 grade în plus a temperaturii fazei solide conduce la mărirea consumului de cocs cu circa 10%.

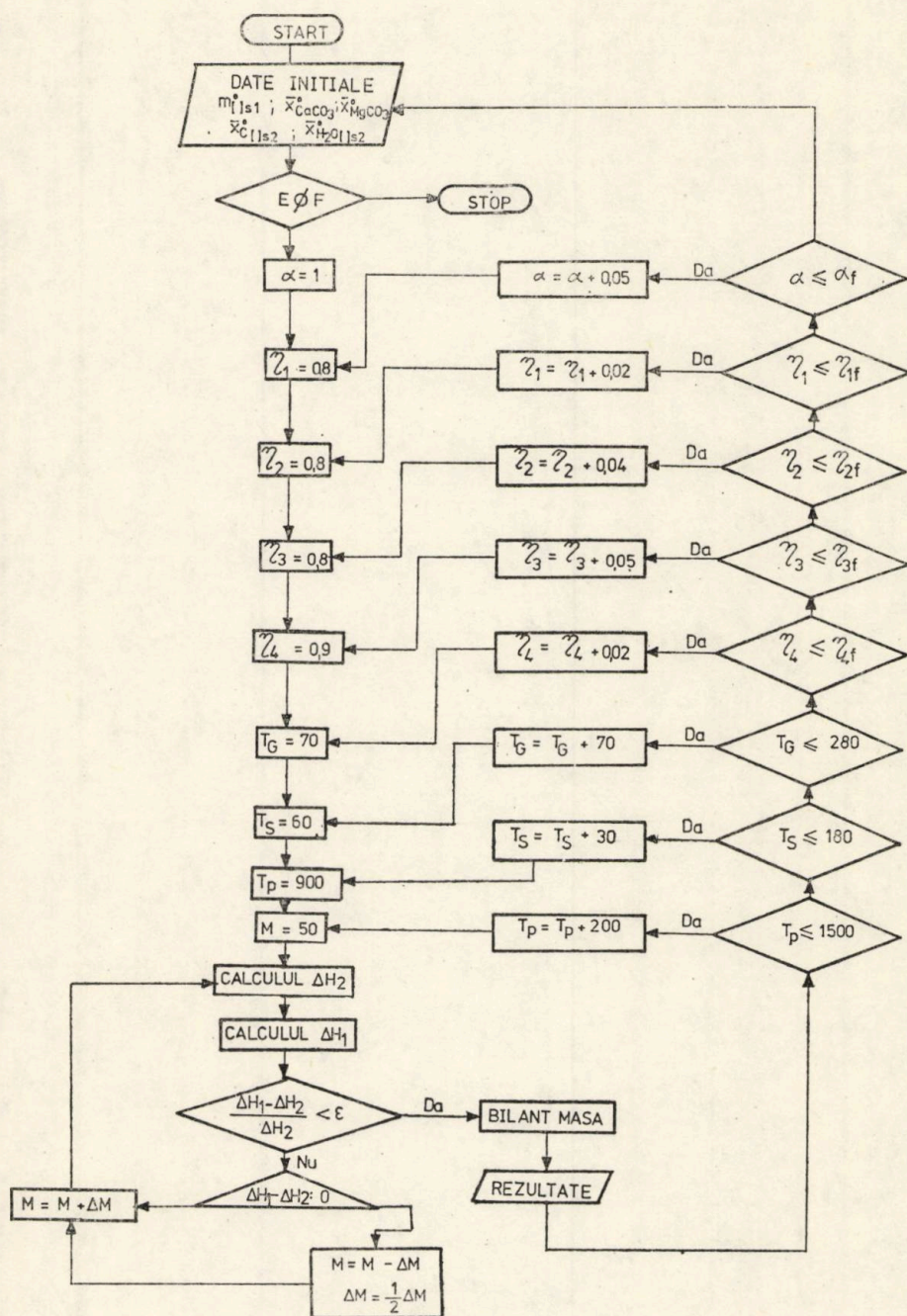
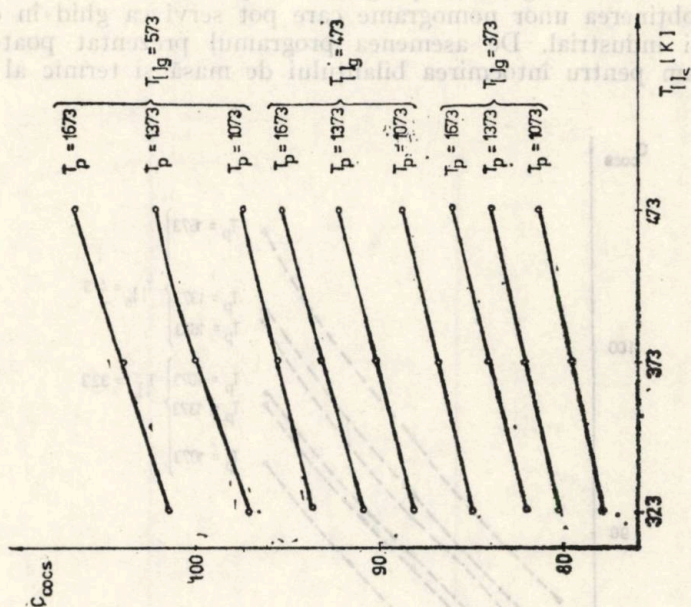
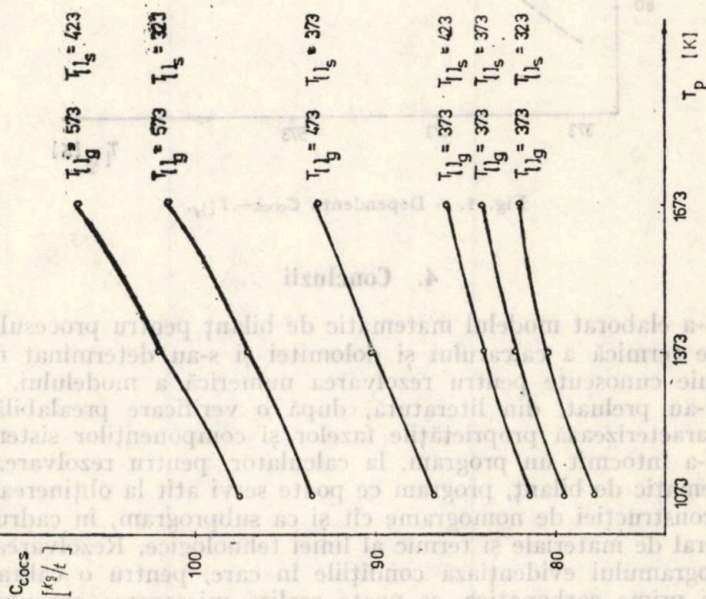


Fig. 1.— Schema logică a programului de rezolvare a modelului matematic de bilanț.

Fig. 3. — Dependenta C_{cocs} — T_p .Fig. 2. — Dependenta C_{cocs} — $T(1)$.

Rezolvarea integrală a programului pentru diverse materii prime permite obținerea unor nomograme care pot servi ca ghid în conducerea procesului industrial. De asemenea programul prezentat poate servi ca subprogram pentru întocmirea bilanțului de masă și termic al liniei tehnologice.

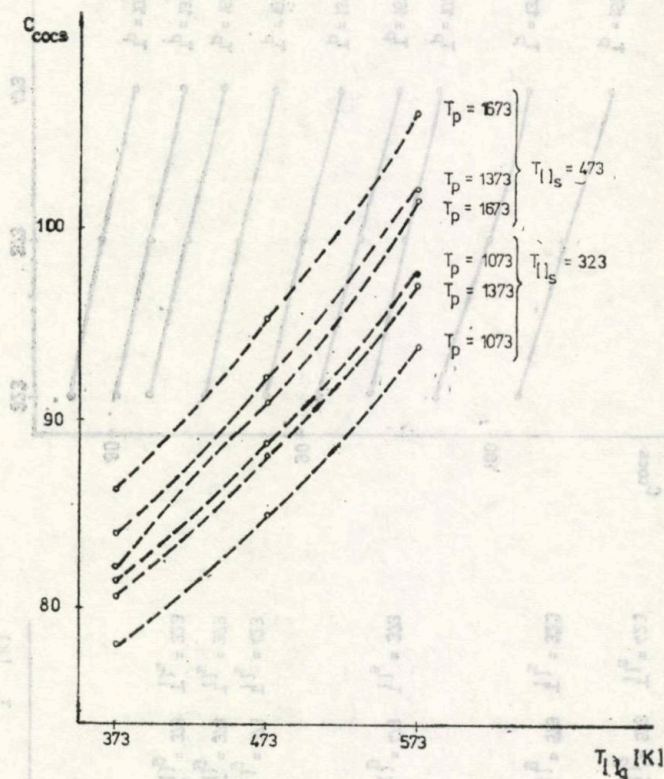


Fig. 4. — Dependența C_{coca} — T_{lg} .

4. Concluzii

1. S-a elaborat modelul matematic de bilanț pentru procesul de descompunere termică a calcarului și dolomitei și s-au determinat mărimile care trebuie cunoscute pentru rezolvarea numerică a modelului.
2. S-au preluat, din literatură, după o verificare prealabilă, mărimile ce caracterizează proprietățile fazelor și componentilor sistemului.
3. S-a întocmit un program, la calculator, pentru rezolvarea modelului matematic de bilanț, program ce poate servi atât la obținerea datelor necesare construcției de nomograme cât și ca subprogram, în cadrul bilanțului general de materiale și termic al liniei tehnologice. Rezolvarea numerică a programului evidențiază condițiile în care, pentru o calitate dată a materiei prime carbonatice, se poate realiza micșorarea consumului de combustibil.

4. S-a rezolvat bilanțul de materiale și termic cu ajutorul unui calculator, datele obținute s-au generalizat, stabilindu-se tipurile principale de dependențe pe baza cărora rezultă condițiile de micșorare a consumului de combustibil.

Notății

X_{A_i}	— fracții molare, volumice, de componenți,
$\bar{X}_{A_i}$	— fracții masice de componenți,
V_{A_i}	— volum de componenți,
m_{A_i}	— masa de componenți,
s, l, g	— simbolul fazei pentru solid, lichid, gaz,
V_M	— volum molar,
A_i	— suprafața zonelor cuptorului, $[m^2]$,
$T_{[s]}$	— temperatura fazei solide la ieșirea din cuptor,
$T_{[g]}$	— temperatura fazei gazoase la ieșirea din cuptor,
T_p	— temperatura procesului,
C_p	— căldura specifică,
α	— coeficientul excesului de aer,
η_{A_i}	— grad de transformare,
$\Delta H_{p,pt}$	— pierderi specifice de căldură prin pereți,
$\Delta H_{vap,(T)}$	— efectul termic în procesul de vaporizare a apei,
A''_i	— simbolul inertelor din fazele reactant și fazele produse de reacție,
M	— masa cocsului,

$$\Delta H_1 = Q_{[s_1]}^0 + Q_{[l_1]}^0 + Q_{[g]}^0 + \Delta_R H_T.$$

$$\Delta H_2 = Q_{[s]} + Q_{[g]} + \Delta_R H_T + Q_{vap}.$$

Indici

0	— mărimi ce se referă la intrare,
$[s_1]$	— faza solidă (calcar sau dolomită),
$[s_2]$	— cocs,
$[s]$	— var sau var dolomitic,
$[g]$	— faza gazoasă.

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DETERMINATION OF COKE SPECIFIC CONSUMPTION DURING LIME AND DOLOMITE DECOMPOSITION PROCESS

(Summary)

The utilisation possibilities of balance mathematical model for the determination of fuel specific consumption during lime decomposition process is studied.

On the basis of this industrial process analysis, mass and thermal balance equations were performed, valuable both for lime and dolomite.

The method was established to be able for the computer solution of the balance mathematic model for the determination of coke consumption, showing, also, the utilisation possibilities of the performed program.

THEORETICAL STUDY ON THE IONIC POLYMERIZATION OF N-PENTENYLCARBAZOLE (NPC)

BY

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1. Introduction

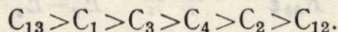
In a previous paper [1] the radicalic polymerization of NPC was studied. Using AIBN and DTBP as initiators, polymers with low degrees of polymerization was obtained. The MO and perturbation theory data with experimental results were correlated.

3 Results and Discussion

In what follows, a theoretical study regarding the ionic polymerization of NPC was performed in order to anticipate the experimental data. Extended Hückel uniterate (EH) method was used for the calculation of atomic charges, atomic orbital coefficients and MO energies. The geometry of the NPC molecule was presented in a previous paper [1].

The total atomic charges in the NPC molecule are given in Fig. 1.

Depending on these data, the following order in a charge controlled reaction with an electrophilic reagent can be established [2], [3]:



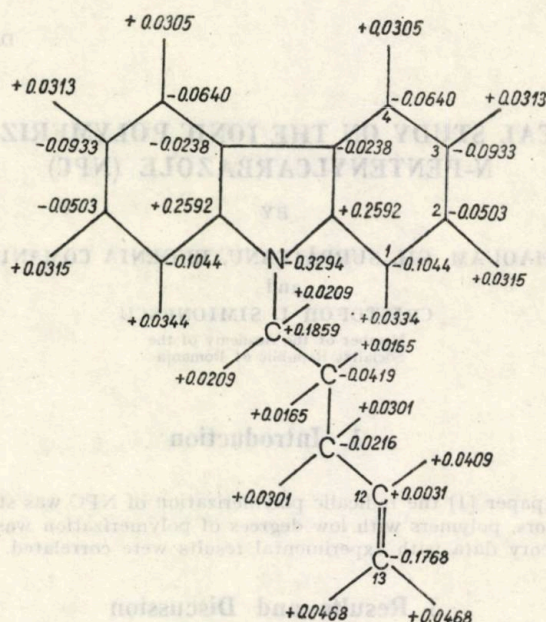
The same atoms are disposed in an inverse order in a charge controlled reaction with nucleophilic reagents.

To obtain more accurate results on the ionic polymerization of NPC, the study of the interaction between the NPC-molecule with NPC-cation and -anion was carried out.

The geometries of NPC-cation and -anion used in the calculations are similar to that of NPC-molecule, excepting the double bond. The C_{13} atom is tetrahedral in both NPC-ions; the length of single $C_{12}-C_{13}$ bond is 1,50 Å and the C_{12} atom is trigonal. Through a proton or hydrure ion addition to the NPC-molecule, the NPC-ions were formed.

Figs. 2 and 3 present the total atomic charges in the NPC-cation and -anion, respectively.

From the spatial representation of these molecular species, the interactions occur between C_{12} (p_x orbital) from the cation (anion) and C_{12} , C_{13} (p_x orbital) or C_1 , $C_2, \dots, C_4$ (p_z orbital) from NPC. The interactions are con-



$$E_T = -1607.855 \text{ eV}$$

Fig. 1. — Total atomic charges in the NPC-molecule.

sidered to be of donor—acceptor type. Thus, the following equation from the perturbation theory [4] can be applied:

$$\Delta E = \frac{q_a q_b}{R_{ab} \epsilon} + 2 \sum_r \sum_s \frac{(C_{ra} C_{sb} \beta_{ab})^2}{E_r^* - E_s^*},$$

where: q_a and q_b are the total charges of the interacting atoms a of donor R and b of acceptor S ; ϵ — the effective dielectric constant of the medium; R_{ab} — the distance between the two atoms, a and b ; C_{ra} — the coefficients of the atomic orbitals a in the occupied molecular orbitals r ; C_{sb} — the coefficients of the atomic orbitals b in the unoccupied molecular orbitals s ; β_{ab} — the resonance integral between the interacting atomic orbitals a and b ; E_r^* , E_s^* — quantities related to the energy of the molecular orbitals r and s of the isolated R and S molecules.

Using this equation, the interaction energies ΔE are calculated. The E_r^* and E_s^* energies were replaced by the energies of the molecular orbitals E_r and E_s , respectively.

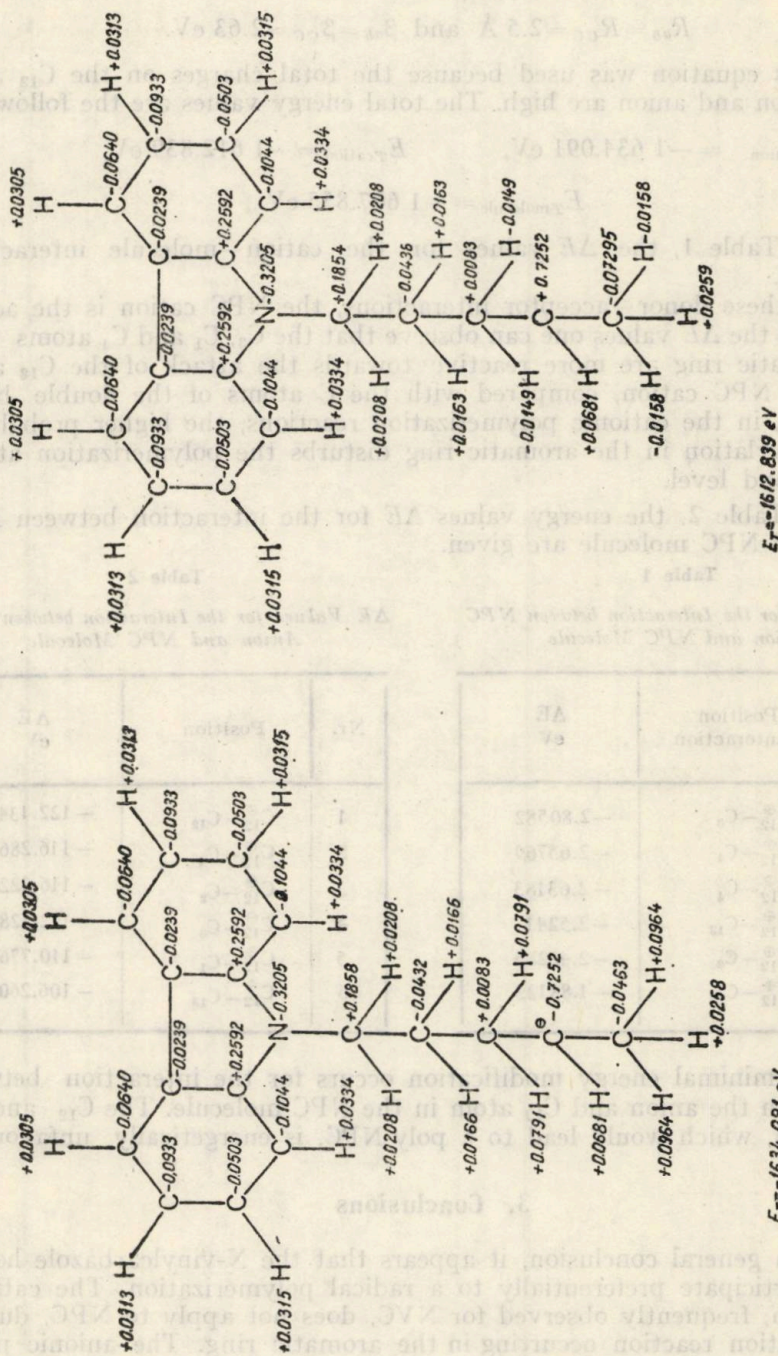


Fig. 2. — Total atomic charges in the NPC-cation.

$$E_T = -1612.839 \text{ eV}$$

Fig. 3. — Total atomic charges in the NPC-anion.

Other considered values [5], [6] are the following:

$$R_{ab}=R_{cc}=2.5 \text{ \AA} \text{ and } \beta_{ab}=\beta_{cc}=2.63 \text{ eV.}$$

This equation was used because the total charges on the C_{12} atom from cation and anion are high. The total energy values are the following:

$$E_{T\text{anion}} = -1\,634.091 \text{ eV,} \quad E_{T\text{cation}} = -1\,612.839 \text{ eV,}$$

$$E_{T\text{molecule}} = -1\,607.855 \text{ eV.}$$

In Table 1, the ΔE values for the cation—molecule interactions are given.

In these donor—acceptor interactions, the NPC cation is the acceptor. From the ΔE values one can observe that the C_3 , C_1 and C_4 atoms from the aromatic ring are more reactive towards the attack of the C_{12} atom from the NPC cation, compared with the C atoms of the double bond. Therefore, in the cationic polymerization reactions, the higher probability of the alkylation in the aromatic ring disturbs the polymerization at the double bond level.

In Table 2, the energy values ΔE for the interaction between NPC anion and NPC molecule are given.

Table 1

ΔE Values for the Interaction between NPC Cation and NPC Molecule

Nr.	Position of interaction	ΔE eV
1	$C_{12}^{\oplus}-C_3$	-2.80582
2	$C_{12}^{\oplus}-C_1$	-2.65769
3	$C_{12}^{\oplus}-C_4$	-2.63183
4	$C_{12}^{\oplus}-C_{13}$	-2.5241
5	$C_{12}^{\oplus}-C_2$	-2.45285
6	$C_{12}^{\oplus}-C_{12}$	-1.88123

Table 2

ΔE Values for the Interaction between NPC Anion and NPC Molecule

Nr.	Position	ΔE eV
1	$C_{12}^{\ominus}-C_{12}$	-122.1346
2	$C_{12}^{\ominus}-C_4$	-116.2861
3	$C_{12}^{\ominus}-C_2$	-116.0226
4	$C_{12}^{\ominus}-C_3$	-112.1283
5	$C_{12}^{\ominus}-C_1$	-110.7764
6	$C_{12}^{\ominus}-C_{13}$	-106.2607

The minimal energy modification occurs for the interaction between C_{12} atom in the anion and C_{12} atom in the NPC molecule. The C_{12} and C_{13} interaction, which would lead to a poly-NPC, is energetically unfavoured.

3. Conclusions

As a general conclusion, it appears that the N-vinylcarbazole homologues participate preferentially to a radical polymerization. The cationic mechanism, frequently observed for NVC, does not apply to NPC, due to the alkylation reaction occurring in the aromatic ring. The anionic polymerization is energetically unfavoured.

The attempts to polymerize NPC with cationic and anionic initiators as BF_3 , TiCl_4 , respectively buthyl litium and sodium-naphthyl were proved to be unsuccessful.

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STUDIUL TEORETIC AL POLIMERIZĂRII IONICE A N-PENTENILCARBAZOLULUI (NPC)

(Rezumat)

Folosind metoda Hückel extins, neiterativ și teoria perturbației, s-a întreprins un studiu al polimerizării ionice a N-pentenilcarbazolului (NPC). Atomii de C de la legătura dublă sint mai puțin reactivi decât atomii de C din inelul aromatic. Calculele teoretice sugerează faptul că NPC nu se pretează la o polimerizare ionică. Datele experimentale confirmă rezultatele teoretice.

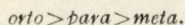
THE USING OF EXTENDED HÜCKEL METHOD FOR THE DETERMINATION OF THE XYLENES ISOMERISATION DIRECTION

BY

N. NAUM, GH. SURPĂȚEANU, V. ABABÎ, FLORIN VITAN
and MIRCEA CONSTANTINESCU

1. Introduction

In a previous paper [1], based on a theoretical study and using the CNDO/2 procedure method, was found that in alkylation reaction of toluene with methanol the substitution of the methyl group of toluene is:



In alkylation of toluene with methanol over synthetic zeolites [2], at different temperatures, the content of *meta*-xylene in reaction mixture increase with the temperature.

Since the faujazitic catalysts, activated at different temperatures, have been either Brønsted or Lewis acidity [3], in alkylation of toluene, the alcohol can interact with catalyst by the oxygen pair of electrons, making easily the elimination of water and carbocation formation.

This considerations justify our theoretical study [1] and determined us to take in study the process of xylenes isomerisation.

2. The Calculation of Reactivity Functions

For the begining, we have as purpose the calculus of the orbital molecular energies of the atomic orbitals. Coefficients of molecular orbitals and the total atomic charges of the atoms in *orto*-, *meta*- and *para*-xylene, using the EHMO procedure method (Extended Hückel Molecular Orbital), are also determined.

The geometries of xylene molecules were approximated as follow: the benzene ring was considered plane, having only trigonals carbon atoms, with angles of 120° . The exocycle atoms are tetragonals with angles of $109^\circ 28'$. The distances between cyclic carbon atoms are 1.50 Å. All distances C—H are equal to 1.09 Å. The calculations of molecular orbitals were performed on a Felix C-256 computer. The total atomic charges of atoms in *orto*-, *meta*- and *para*-xylene are represented in Fig. 1 a...c.

We consider that all atoms belonging to the above molecules have positive or negative atomic charges of law values. The Brønsted or Lewis acid catalyst could act on the xylene molecules, inducing an electronic movement, even in the aromatic ring.

An electronic movement to trigonale carbon atoms adiacents to the trigonale carbon atoms, bonded to tetragonale exocyclic carbon, could be considered as being the reason of isomerisation reaction.

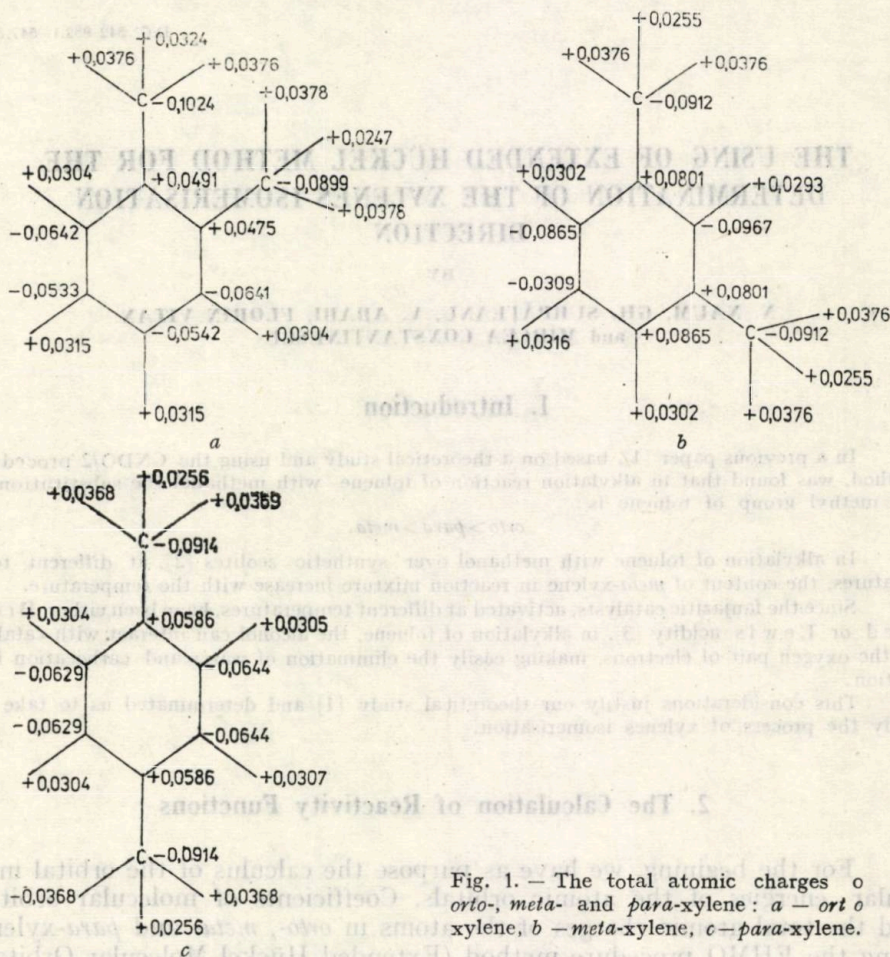


Fig. 1. — The total atomic charges o
ortho-, meta- and para-xylene: a — ort o
xylene, b — meta-xylene, c — para-xylene.

We have also calculated the interaction energies between the P atomic orbital of the tetragonal carbon atom, noted by asterisc, and the $P(\pi)$ orbital of the adjacent trigonal carbon atom, noted by two asterisks. The interactions taken in consideration are presented in Fig. 2 a...c. The interaction energy between two molecules, S and T , by their A and B atoms, respectively, is calculated with the relation:

$$(1) \quad \Delta E = \frac{Q_A Q_B}{\epsilon R_{AB}} + 2 \sum_S^{\text{occ.}} \sum_T^{\text{unocc.}} + \sum_S^{\text{unocc.}} \sum_T^{\text{occ.}} \frac{(C_A C_B \beta_{AB})^2}{E_m - E_n},$$

where: Q_A and Q_B represents the total atomic charges on the interacting A and B atoms; ϵ — the locale dielectric constant; R_{AB} — the distance between A and B atoms; C_A and C_B — the atomic orbital coefficients of

A and B atoms; β_{AB} — the resonance integrals between atomic orbitals belonging to A and B atoms; E_m — the double occupied (occ.) molecular orbitals; E_n — the unoccupied (unocc.) molecular orbitals.

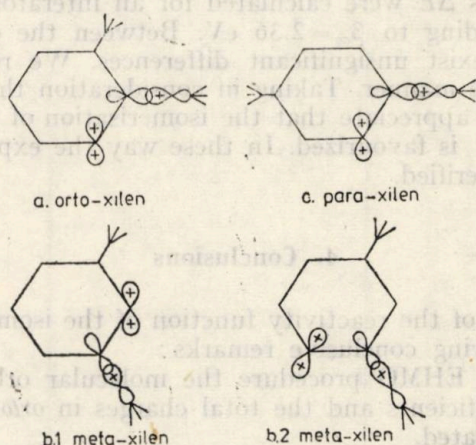


Fig. 2. — The orbital interactions for: a — *ortho*-xylene, b_1 and b_2 — *meta*-xylene, c — *para*-xylene.

The summations $\sum_S^{\text{occ.}}$ and $\sum_S^{\text{unocc.}}$ correspond to the occupied and unoccupied molecular orbitals in molecule S and similarly for the summations $\sum_T^{\text{occ.}}$ and $\sum_T^{\text{unocc.}}$, in the molecule T .

In our case since take place a isomerisation, the xylene molecule is both acceptor or donor of electrons.

Next, the energies for the specified interaction presented in Fig. 2 are calculated. The calculus were performed as in the general scheme represented in Fig. 3.

3. Results and Discussions

The proposed relation (1) is a simplified form of the general equation proposed by Klapman and Solem [4], [5].

Table 1

The Interaction Energies, ΔE

Nr.	Interaction	ΔE eV
1	a	-0.8094
2	b_1	-0.7912
3	b_2	-0.7983
4	c	-0.8096

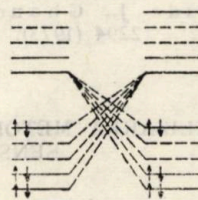


Fig. 3. — The interaction between occupied and unoccupied orbitals in xylene.

In the Table 1, the interaction energies for the above isomerisation are given.

For obtaining numerical values, we have considered that $\epsilon=1$. The interaction energies ΔE were calculated for an interatomic distance $R_{cc}=2.5 \text{ \AA}$, corresponding to $\beta_{cc}=2.36 \text{ eV}$. Between the obtained values of the energies ΔE exist insignificant differences. We recommend their use only in a qualitative manner. Taking in consideration the results presented in Table 1 we can appreciate that the isomerisation of *orto*- and *para*-xylene to *meta*-xylene is favoured. In these way the experimental data obtained in [2] are verified.

4. Conclusions

The calculus of the reactivity function of the isomerisation of xylene leads to the following conclusive remarks:

a) Using the EHMO procedure the molecular orbitals energies, the atomic orbital coefficients and the total charges in *orto*-, *meta*-, and *para*-xylene were calculated.

b) The theoretical results prove the existence of an isomerisation process from *orto*- and *para*-xylene to *meta*-xylene.

c) In the alkylation process of toluene with methanol the *meta*-xylene could be obtained by isomerisation.

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UTILIZAREA METODEI HÜCKEL EXTINS ÎN VEDEREA DETERMINĂRII SENSULUI DE IONIZARE A XILENILOR

(Rezumat)

Utilizând metoda orbitalilor moleculari Hückel extinși s-a determinat sensul izomerizării xilenilor.

S-au calculat funcțiile de reactivitate pentru *orto*-, *meta*- și *para*-xilen, utilizând un calculator Felix C-256.

LA SYNTHÈSE DE QUELQUES NOUVEAUX DÉRIVÉS DE LA DL-MÉTHIONINE

PAR

C. H. BUDEANU et SVETLANA COLCERU-MIHUL

1. Introduction

La synthèse de quelques dérivés des α -amino-acides naturels contenant de certaines groupes, particulièrement des groupements ayant un effet pharmacodynamique, présente une exceptionnelle importance ayant en vue qu'on puisse obtenir des substances biologiquement actives, avec une toxicité diminuée, véhiculés facilement au niveau des cellules et maintenues plus longtemps dans l'organisme.

Dans les travaux antérieurs [1]...[8] l'un de nous a obtenu une série de dérivés des acides asparagique et glutamique, tant à la groupe amino, qu'à la groupe carboxylique, ainsi qu'à toutes les deux groupes, parmi lesquels quelques uns exercent une activité antimicrobienne et antifongique.

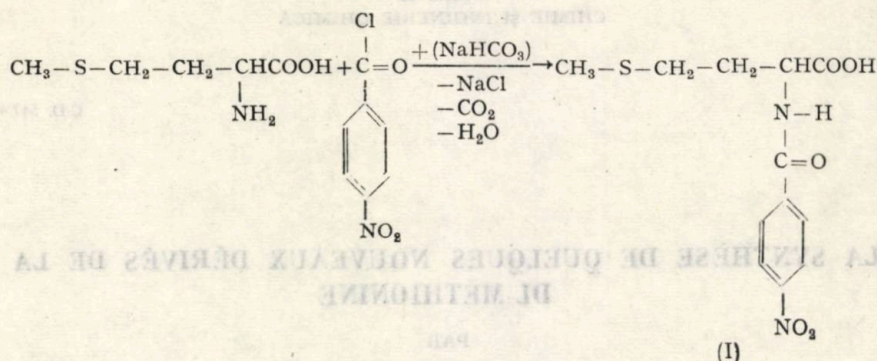
Dans une autre série de travaux [9]...[20] l'un de nous a greffé sur certains dérivés des acides asparagique et glutamique le groupement azote-ypéritique, en obtenant par cette voie des substances nouvelles anticancéreuses ayant une appréciable activité cytostatique et une toxicité relativement réduite.

Parmi les amino-acides très importants pour l'organisme on considère aussi la méthionine, qui appartient aux α -amino-acides essentiels, étant indispensable pour l'homme bien que pour les animaux, grâce à son rôle dans le processus de transméthylation et de transsulfuration, ainsi que dans la formation des érythrocytes.

Compte tenu de son rôle important dans l'organisme, la méthionine ainsi que certains dérivés fonctionnels de celle-la, sont utilisés, en particulier, dans le traitement de quelques affections hépatiques. Dans ce qui suit on étudie la synthèse de quelques nouveaux dérivés de l'acide DL- α -amino- γ -méthylthiobutyrique en vue d'établir la corrélation entre la structure chimique et les propriétés biologiques.

2. Considérations théoriques

Nous avons préparé tout d'abord l'acide DL- α -[N-(*o*-nitrobenzoyl)amino]- γ -méthylthiobutyrique (I) par l'acylation de la DL-méthionine dans une solution aqueuse de bicarbonate de sodium avec le chlorure de l'acide *p*-nitrobenzoïque dissous en benzène, selon le schéma :



La structure de ce produit de condensation a été établie par l'analyse chimique élémentaire et confirmée à l'aide des spectres IR.

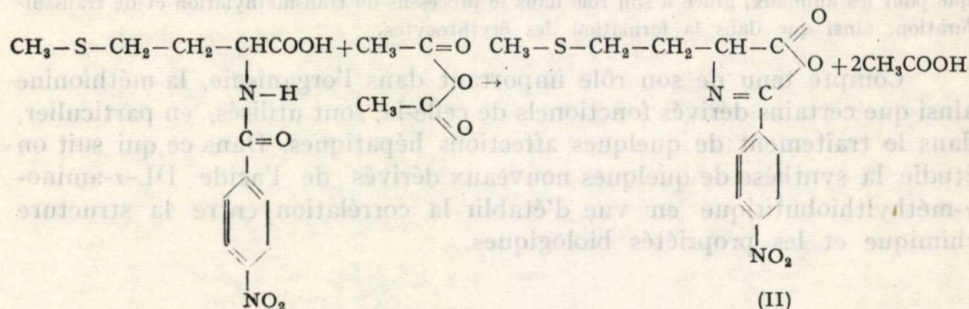
Dans le spectre IR il y a une bande à $3\,310\text{ cm}^{-1}$ due à la vibration de la groupe $-\text{NH}$, et à $1\,730\text{ cm}^{-1}$ une bande caractéristique à la groupe carbonyle. La bande située à 725 cm^{-1} correspond au groupement thioétherique.

Par récrystallisation dans l'eau l'acide- α -[N-(*p*-nitrobenzoyl) amino]- γ -méthylthiobutyrique fond à $170^\circ\text{...}171^\circ\text{C}$.

Le point de fusion de ce produit a été établi à $191^\circ\text{...}192^\circ\text{C}$ par E. Ronwin [21], à $169^\circ\text{...}170^\circ\text{C}$ par F. E. King et collaborateurs [22] et à $170^\circ\text{...}171^\circ\text{C}$ par W. B. Wright jr. et collaborateurs [23].

Évidemment que le point de fusion indiqué par E. Ronwin [21] n'est pas exact.

Le traitement à chaud de l'acide DL- α [(N-*p*-nitrobenzoyl) amino]- γ -méthylthiobutyrique avec l'anhydride acétique conduit à l'élimination d'une molécule d'eau et à la fermeture d'un cycle de cinq atomes entre la groupe carboxylique et le groupement aminique acylé, en résultant ainsi la DL-2-*p*-nitrophényl-4- β -méthylthioéthyl-5-oxazolone (II), selon le schéma:



En ce qui concerne le mécanisme de la fermeture du cycle oxazolonique sous l'action de l'anhydride acétique, celui-ci débute par le protonage de l'atome d'oxygène non carbonyle de l'anhydride acétique et s'ensuit, probablement, par la formation d'une anhydride mixte. L'anhydride mixte se transforme ensuite en oxazolone par l'élimination de l'anion acétoxy, simultanément avec l'attaque nucléophile sur l'atome de carbon carboxy-

sence d'une bande dans la région de $3\,350\text{ cm}^{-1}$, qui correspond au groupement amidique. On constate que dans la région de $1\,800\text{ cm}^{-1}$ il n'y a aucune bande caractéristique au groupement fonctionnel d'anhydride, ce qui prouve qu'à l'ouverture du cycle oxazolone, l'acide *p*-aminobenzoïque a réagi par la groupe aminique et non pas par le groupement carboxylique. En vue d'appuyer le schéma supposé pour cette réaction, on a enregistré aussi le spectre IR du produit de la réaction entre l'oxazolone et l'ester éthylique de l'acide *p*-amino-benzoïque. On constate aussi que ce spectre a, en général, une allure similaire au celui du composé amidique, résulté par la réaction de l'oxazolone avec l'acide *p*-aminobenzoïque.

Les bandes des deux spectres situées à $1\,550\text{ cm}^{-1}$ et respectivement à $1\,350\text{ cm}^{-1}$, correspondent à la groupe nitrique qui est liée au noyau benzénique tandis que la bande de 725 cm^{-1} est caractéristique au groupement thioéthérique. L'étude des spectres IR confirme les structures proposées sur la base des analyses chimiques des composés à fonction d'amide obtenus par l'ouverture du cycle oxazolone.

3. Partie expérimentale

3.1. L'acide DL- α [N(*p*-nitrobenzoyl)amino]- γ -méthylthiobutyrique (I)

Dans un ballon de 600 ml muni d'un agitateur mécanique, on introduit, à la température ambiante, 5 g de DL-méthionine dans 90 ml d'eau et 17 g de bicarbonate de sodium. On agite jusqu'à l'obtention d'une solution homogène et ensuite on introduit, pendant 30 min, 8 g de chlorure de l'acide *p*-nitrobenzoïque dissous dans 30 ml de benzène.

Après avoir ajouté la quantité entière de solution benzénique on constate la formation d'une petite quantité de précipité de couleur blanche-jaunâtre. On poursuit l'agitation encore une heure, on filtre à vide et on ajoute encore 30 ml d'eau, pour ressoudre la quantité entière du produit solide. On enlève, premièrement, la couche benzénique du filtrat par un entonnoir de séparation ayant un pH=2,5, quand on observe la séparation d'un précipité volumineux de couleur blanche, qui est filtré à vide et lavé sur le filtre avec de l'eau distillé. Le produit brut, sec, fond à $168^\circ\text{--}170^\circ\text{C}$. Par recristallisation, dans l'eau bouillante et séchage, le produit fond à $170^\circ\text{--}171^\circ\text{C}$. Le rendement est d'environ 88%.

Le produit est soluble, à froid, dans l'alcool méthylique et éthylique, dans l'acétone, le chloroforme, l'acétate de butyle et dans la diméthylformamide. Il est soluble dans l'eau, seulement à chaud. Il est insoluble dans le benzène, l'éther éthylique et dans l'éther de pétrole.

Analyses :	$\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_5\text{S}$	C%	H%	N%	S%
Calculé :		48,32	4,69	9,39	10,74
Trouvé :		48,60	4,79	9,50	10,78
		48,42	4,53	9,39	10,97

Spectre IR (KBr): $3\,310\text{ cm}^{-1}$, $\nu_{\text{N-H}}$ amidique;
 $1\,730\text{ cm}^{-1}$, $\nu_{\text{C=O}}$; 725 cm^{-1} ; $\nu_{\text{S-}}$.

3.2. DL-2-*p*-nitrophényl-4- β -méthylthioéthyl-5-oxazolone (II)

On chauffe sur bain-marie pendant 30 min, dans un ballon de 50 ml muni d'un réfrigérant à l'eau, une quantité de 5 g d'acide DL- α (*p*-nitrobenzoylamino)- β -méthylthiobutyrique avec 16 ml d'anhydride acétique. Le produit de la réaction est introduit, peu-à-peu, sous agitation, dans un mélange formé par 50 ml éther de pétrole et 10 ml éther éthylique. On continue l'agitation pendant une heure, on enlève le liquide par décantation et ensuite le produit solide est lavé plusieurs fois avec de l'éther de pétrole jusqu'à la disparition de l'opalescence du liquide de lavage. On le filtre à vide, on le lave à l'éther de pétrole et on le sèche. Le produit obtenu fond à $78^\circ\text{--}79^\circ\text{C}$. Il est soluble dans l'acétone, le dioxane et la diméthylformamide. Il est insoluble dans le benzène, l'éther éthylique, l'éther de pétrole et l'acétate de butyl.

Analyses :	$C_{12}H_{12}N_2O_4S$	C%	H%
Calculé :		51,42	4,32
Trouvé :		52,09	4,60
		51,88	4,46

Spectre IR (KBr) : 1800 cm^{-1} , ν_{C-O-C} ; 1700 cm^{-1} , $\nu_{C=N}$;
 $1535, 1350\text{ cm}^{-1}$, ν_{NO_2} ; 725 cm^{-1} , ν_{S-} .

3.3. *o*-Carboxyanilide de l'acide DL- α -[N(*p*-nitrobenzoyl)amino]- γ -méthylthiobutyrique (III)

Dans un ballon pourvu d'un réfrigérant ascendant on introduit 1,4 g de DL-2-*p*-nitro-phényl-4-(β -méthylthioéthyl)-5-oxazoline dissous dans 15 ml de dioxane et 0,7 g d'acide *o*-aminobenzoïque. Le ballon doit être chauffé pendant 4 h dans un bain d'acide sulfurique à la température de $115^\circ\text{...}120^\circ\text{C}$. Après l'élimination du dioxane par distillation il reste un produit solide de couleur blanche qui fond à $212^\circ\text{...}214^\circ\text{C}$. Par récrystallisation, dans le dioxane, à chaud, le produit fond à $213^\circ\text{...}214^\circ\text{C}$.

Le produit est soluble dans l'acétone, dans le dioxane et dans la diméthylformamide, mais insoluble dans l'eau, l'éther éthylique et dans l'éther de pétrole.

Analyses :	$C_{19}H_{19}N_3O_6S$	C%	H%
Calculé :		54,73	4,60
Trouvé :		54,86	4,56
		54,62	4,73

3.4. *m'*-Carboxyanilide de l'acide DL- α -[N(*p*-nitrobenzoyl)amino]- γ -méthylthiobutyrique (IV)

On la prépare selon la méthode décrite pour la *o'*-carboxyanilide. Le produit fond à $252^\circ\text{...}254^\circ\text{C}$.

Analyses :	$C_{19}H_{19}N_3O_6S$	C%	H%
Calculé :		54,73	4,60
Trouvé :		54,56	4,69
		54,64	4,74

3.5. *p'*-Carboxyanilide de l'acide DL- α -[N(*p*-nitrobenzoyl)amino]- γ -méthylthiobutyrique (V)

On la prépare selon la méthode décrite pour la *o'*-carboxyanilide. Après la récrystallisation dans l'eau à l'ébullition, le produit fond à $223^\circ\text{...}225^\circ\text{C}$.

Analyses :	$C_{19}H_{19}N_3O_6S$	C%	H%
Calculé :		54,73	4,60
Trouvé :		54,62	4,39
		54,58	4,58

Spectre IR (KBr) : 3350 cm^{-1} , ν_{NH} amidique ; 1550 cm^{-1} , ν_{Ar-NO_2} ;
 725 cm^{-1} , ν_{S-} .

3.6. *p'*-Carboxyanilide de l'acide DL- α -[N(*p*-nitrobenzoyl)amino]- γ -méthylthiobutyrique (VI)

On la prépare selon la méthode décrite pour la *o'*-carboxyanilide. Le produit fond à $167^\circ\text{...}168^\circ\text{C}$.

Analyses :	$C_{21}H_{23}N_3O_6S$	C%	H%
Calculé :		52,62	5,20
Trouvé :		56,17	5,05
		56,32	5,16

3.7. *p*'-Carboxy-*m*'-hydroxyanilide de l'acide DL- α [N-(*p*-nitrobenzoyl)amino]- γ -méthylthiobutyrique (VII)

On la prépare à partir de la DL-2-*p*-nitrophényl-4- β -méthylthioéthyl-5-oxazolone et de l'acide *p*-amino-salicylique selon la méthode décrite pour la *o*'-carboxyanilide. Le produit fond à 137°...138°C.

<i>Analyses</i> :	$C_{19}H_{19}N_3O_5S$	C%	H%
Calculé :		49,29	5,57
Trouvé :		49,31	5,62
		49,42	5,49

3.8. 3'-Carboxypropylamide de l'acide DL- α [N-(*p*-nitrobenzoyl)amino]- γ -méthylthiobutyrique (VIII)

On la prépare à partir de la DL-2-*p*-nitrophényl-4- β -méthylthioéthyl-5-oxazolone et de l'acide γ -aminobutyrique selon la méthode décrite pour la *o*'-carboxyanilide. Après la recrystallisation dans l'eau bouillante le produit fond à 148°...150°C.

<i>Analyses</i> :	$C_{19}H_{21}N_3O_6S$	C%	H%
Calculé :		50,13	5,48
Trouvé :		49,96	5,33
		50,21	5,46

4. Conclusions

a) L'acide DL- α [N-(*p*-nitrobenzoyl)amino]-*p*-butyrique a été préparé par l'acylation de la DL-méthionine avec le chlorure de l'acide *p*-nitrobenzoïque.

b) On a obtenu la 2(*p*-nitrophényl)-4- β -méthylthioéthyl-5-oxazolone par l'action de l'anhydride acétique sur la DL- α N(*p*-nitrobenzoyl)méthionine.

c) On a synthétisé huit amides nouvelles par l'ouverture du cycle 2(*p*-nitrophényl)-4- β -méthylthioéthyl-5-oxazolone sous l'action de certains composés qui contiennent dans la molécule, sauf la groupe de l'amide primaire, encore un groupement carboxylique ou carbétoxylique.

d) La structure des nouveaux produits synthétisés a été établie par analyse élémentaire et confirmée par analyse spectrale en IR.

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SINTEZA UNOR NOI DERIVAȚI AI DL-METIONINEI

(Rezumat)

În scopul obținerii unor noi substanțe cu posibilă activitate fiziologică, s-a sintetizat DL-*p*-nitrobenzoil-metionina, oxazolona respectivă și o serie de opt amide noi prin deschiderea ciclului acestei oxazolone cu unii compuși conținând în moleculă pe lângă grupa de amină primară și o grupare carboxilică sau carbetoxică.

Structura noilor compuși sintetizați s-a stabilit pe baza analizei elementare și a fost confirmată cu ajutorul analizei speciale în IR.

2-HYDROXY-KETONES

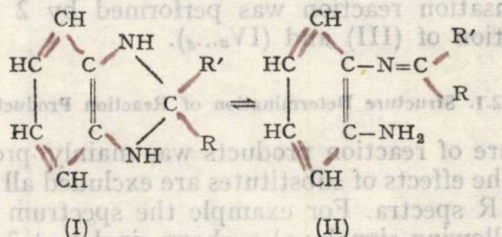
VII. REACTIONS OF SOME *ORTHO*-HYDROXY-ACETOPHENONES
WITH *ORTHO*-PHENYLENEDIAMINE

BY

AL. CAȘCAVAL, VIRGIL BĂRBOIU and BORIS ARVENTIEV

1. Introduction

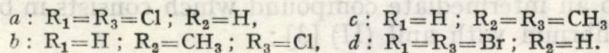
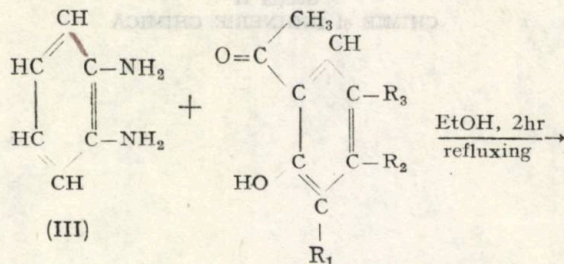
It is known that the Hinsberg's synthesis of benzimidazoles [1], [2] leads to an intermediate compound which consists in benzimidazoline (I) in equilibrium with anil (II) [3]:



In what follows it is proved that the synthesis leads only to anil compounds when one of the substitutes R and R' is an aromatic ring. This conclusion results from the reaction of *ortho*-hydroxy-acetophenone derivatives with *ortho*-phenylene-diamine. N-acetylation and addition at the amine group of obtained anils are also presented.

2. Results and Discussions

Undertaking our studies on the 2-hydroxy-3,5-dichloro-acetophenone (IV_a) reactivity [4], we found that the condensation of this compound with *ortho*-phenylenediamine (III) leads to a pure and unitary compound of anil structure (V_a). The similar compounds (V_{b,c,d}) were also obtained in the reaction of other 2-hydroxy-acetophenones (IV_{b,c,d}) with *ortho*-phenylenediamine:



The condensation reaction was performed by 2 hours refluxing of an alcoholic solution of (III) and (IV_{a...d}).

2.1. Structure Determination of Reaction Products

The structure of reaction products was mainly proved by ¹H-NMR spectroscopy. If the effects of substitutes are excluded all compounds (V_{a...d}) show similar NMR spectra. For example the spectrum of compound (V_a) consists in the following signals: a) a sharp singlet at 2.35 ppm (δ) arising from the methyl protons; b) a broad and deuterable signal at 3.6 ppm arising very probably from the NH₂ protons; c) a multiplet between 6.5 and 7.1 ppm from the four protons of aromatic ring; d) an AB multiplet with δ_A=7.35 ppm, δ_B=7.40 ppm and J_{AB}=2.5 Hz from the two protons of phenolic ring; e) a very broad and deuterable signal at 14.8 ppm arising from one proton.

These spectral parameters correspond very well to the anil structure (V_a) and are unsuitable with a benzimidazoline structure (I) as follows:

1. The chemical shifts of methyl protons agrees with a methyl group attachment at a double bond (as in compound (V)) and not at a saturated carbon (as in benzimidazoline (I)).
2. The anil structure explains in a satisfactory manner the broad signal at 14.8 ppm as arising from the OH-proton which is so much deshielded due to the hydrogen bond with the nitrogen atom of C=N bond. This hydrogen bond is quite strong because it realizes a plane six membered ring.

3. The possibility of an intermediate compound of benzimidazoline $\rightleftharpoons$ anil type is also excluded because the NMR spectra are well defined and stable.

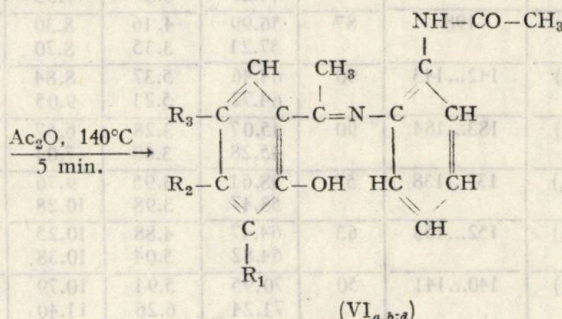
The anil structure of obtained compounds ($V_{a...d}$) is moreover confirmed by the IR absorption spectra mainly by the $1\,620...1\,630\text{ cm}^{-1}$ band assigned to $C=N$ bond.

The spectral and analytical characterization of all compounds (V) is given in the experimental part.

2.2. Reactions at NH_2 Group

Acetylation and addition reactions were performed on the anils (V) to verify the structure and to characterize the amine group reactivity.

a) *N-Acetylation*. The reaction of acetic anhydride with anils ($V_{a,b,d}$) was carried out 140°C for 5 min.:



The structure of obtained compounds was verified by spectral and analytical methods (s. experimental part). The *N*-acetylation is mainly confirmed in the $^1\text{H-NMR}$ spectra by the CO-CH_3 signal at 2.1 ppm (δ) and by the NHCO signal which is placed at 8.1 ppm and sensitive at the spin decoupling from ^{14}N nucleus.

It is to mention that the acetylation reaction using acetic acid instead of acetic anhydride leads to 2-hydroxyacetophenone derivatives ($IV_{a,b,d}$), probably by a Fischer reversion [5].

b) *Reaction with Phenylisothiocyanate*. The reaction takes place by about 5 hours keeping at room temperature the anil and the phenylisothiocyanate dissolved in DMSO or DMF. The reaction product (VII) is obtained with a good yield:

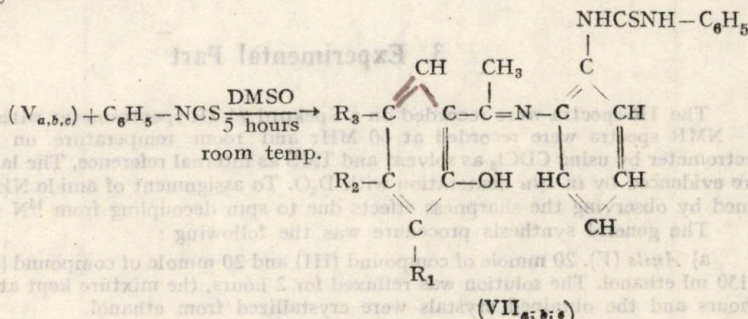


Table 1
Data on Elemental Analysis and IR-Characterization

Compound	M.p. °C	Yield %	%C Calc. Found	%H Calc. Found	%N Calc. Found	%Cl Calc. Found	ν cm ⁻¹
(V _a)	171...172	79	56.95 56.40	4.06 3.65	9.49 10.02	24.04 24.16	3 400, 3 000, 1 620 1 600
(V _b)	138	75	65.59 65.14	5.47 5.37	10.21 10.69	12.91 13.22	3 400, 3 050, 1 630, 1 600
(V _c)	133	20	75.59 76.02	7.08 7.15	11.02 11.18	—	3 400, 3 000, 1 620, 1 600
(V _d)	158...159	67	43.75 44.25	3.12 3.37	7.29 7.53	—	3 400, 3 050, 1 630, 1 600.
(VI _a)	198	87	56.99 57.21	4.16 3.35	8.30 8.70	21.04 21.66	3 420, 3 120, 3 060, 2 920, 1 690, 1 640
(VI _b)	142...143	90	64.46 64.72	5.37 5.21	8.84 9.05	11.19 11.70	3 250, 3 000, 1 670, 1 610
(VI _d)	183...184	90	45.07 45.28	3.28 3.60	6.57 7.01	—	3 400, 3 220, 3 040, 1 690, 1 635, 1 590.
(VII _a)	137...138	57	58.61 58.47	3.95 3.98	9.76 10.28	16.49 16.96	3 100, 3 000, 1 610, 1 590
(VII _b)	152...153	63	64.47 64.82	4.88 5.04	10.25 10.38	8.65 9.01	3 100...2 970, 1 615, 1 590.
(VII _c)	140...141	50	70.95 71.24	5.91 6.26	10.79 11.40	—	3 100...2 900, 1 610, 1 590

The confirmation of structure (VII) was made by using NMR- and IR-spectra and chemical analysis. The appearance of the two thioamide NH groups is undoubtedly shown in the NMR spectra by broad signals at 7.6 and 8.45 ppm, both of them being sensitive at the decoupling from ¹⁴N nuclei.

It is to mention that the reaction of anil (V_a) with phenylisothiocyanate performed after common synthesis of thioureas [6] does not lead to the thiourea derivative (VII_a) but to mixture of thiocarbanilide, ethyl-N-phenyl thiocarbamic acid, 2-hydroxy-3,5-dichloro-acetophenone (IV_a) and an unidentified compound with m.p. 315...317°C.

3. Experimental Part

The IR-spectra were recorded on a Spekdord 71 IR spectrometer with KBr-pellets. The ¹H-NMR spectra were recorded at 60 MHz and room temperature on a JNM-C-60 HL spectrometer by using CDCl₃ as solvent and TMS as internal reference. The labile proton signals were evidenced by *in situ* deuteration with D₂O. To assignment of amide NH signals was confirmed by observing the sharpness effects due to spin decoupling from ¹⁴N nuclei.

The general synthesis procedure was the following :

a) *Anils* (V). 20 mmole of compound (III) and 20 mmole of compound (IV) were dissolved in 150 ml ethanol. The solution was refluxed for 2 hours, the mixture kept at 0...5°C for about 4 hours and the obtained crystals were crystallized from ethanol.

Table 2

¹H-NMR Characterization

Compound	Chemical shifts in δ (ppm), shape*), intensity and assignement of signals
(V _a)	2.30 (s, 3H, CH ₃ =CN); 3.6(bs, 2H, NH ₂); 6.6...7.1 (m, 4H, aromatic); 7.35...7.40 (AB m, 2H, aromatic); 14.8(bs, 1 H.OH).
(V _b)	2.25 (s, 3H, CH ₃ Ph); 2.30 (s, 3H, CH ₃ C=N); 3.6(bs, 2H, NH ₂); 6.6...7.1 (m, 5H, aromatic); 7.65 (s, 1H, aromatic); 14.8 (bs, 1H, OH)
(V _c)	2.25 (s, 6H, CH ₃ Ph); 2.30 (s, 3H, CH ₃ C=N); 3.5 (bs, 2H, NH ₂); 6.7...7.1 (m, 5H, aromatic); 7.4(s, 1H, aromatic); 14.6(bs, 1H, OH).
(V _d)	2.30 (s, 3H, CH ₃ C=N); 3.4(bs, 2H, NH ₂); 6.7...7.2 (m, 4H, aromatic); 7.80(ABm, 2H, aromatic); 14.6 (bs, 1H, OH).
(VI _a)	2.10(s, 3H, CH ₃ CO); 2.40(s, 3H, CH ₃ C=N); 7.2...7.5(m, 4H, aromatic); 7.7(ABm, 2H, aromatic); 8.2 (bs, 1H, NHCO); OH signal is not observable perhaps due to an exaggerated broadening.
(VI _b)	2.10(s, 3H, CH ₃ CO); 2.35(s, 3H, CH ₃ Ph); 2.40(s, 3H, CH ₃ C=N); 6.95(s, 1H, aromatic); 7.2...7.4(m, 4H, aromatic); 7.65(s, 1H, aromatic); 8.3(bs, 1H, NHCO); OH is also not observable as for compound (VI).
(VI _d)	2.10(s, 3H, CH ₃ CO); 2.40(s, 3H, CH ₃ C=N); 7.2...7.4(m, 4H, aromatic); 7.8(ABm, 2H, aromatic); 8.2(bs, 1H, NHCO); OH not observable.
(VII _a)	2.30(s, 3H, CH ₃ C=N); 6.7...8.0(m, 11H, aromatic); 7.6(bs, 1H, NHCS); 8.5(bs, 1H, NHCS); 15.4(bs, 1, H OH).
(VII _b)	2.25(s, 3H, CH ₃); 2.40(s, 3H, CH ₃); 6.5...7.3(m, 11H, aromatic); 7.6(bs, 1H, NHCS); 8.4(bs, 1 H, NHCS); 14.2(bs, 1H, OH).
(VII _c)	2.30(s, 3H, CH ₃); 2.35(s, 3H, CH ₃); 6.8...8.0(m, 11H, aromatic); 7.6(bs, 1H, NHCS); 8.5(bs, 1H, NHCS); 14.0(bs, 1H, OH).

*) s—singlet; bs—broad singlet; m—multiplet.

b) *N-Acetyl derivatives* (VI). 1 mmole of compound (V) together with 5 ml acetic anhydride were heated at 140°C for 5 min. Some yellow crystals appeared when the reaction mixture was diluted with 100 ml water. The purification was made by crystallization from ethanol.

c) *Thiourea derivatives* (VII). 1 mmole of compound (V) together with 1 mmole of phenylisothiocyanate dissolved into 5 ml DMSO (or DMF) were placed into a flask fitted with a stopper and kept at room temperature for 5 hours. The solution was diluted with 25 ml of water. The obtained crystals were crystallized from ligroine.

In the Tables 1 and 2 the experimental results are presented.

3. Conclusions

The anils (V) and their derivatives ((VI) and (VII)) are obtained with good yields.

Taking into account that the molecules of these compounds consist of various complexing groups, namely —OH, —NH₂, C=N—, —NHAc, —NHCSNH—, it is expected to be used like analytical reagents for many cations. Their good complexing properties correspond well to the unusually deshielding ($\delta=10...15$ ppm) of OH proton.

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2-HIDROXI-CETONE

VII. Reacții ale unor *orto*-hidroxi-acetofenone cu *orto*-fenilendiamina

(Rezumat)

Se arată că reacția dintre *orto*-hidroxi-acetofenone și *orto*-fenilendiamină conduce la compuși puri de tip anil. Elucidarea structurii compușilor s-a realizat atât prin spectroscopie RMN cit și prin reacții chimice la gruparea amino. Sint prezentate, de asemenea, procedeele de sinteză, caracterizarea analitică și spectrală a anililor și a derivaților lor (obținuți prin reacția de acetilare sau prin reacția cu izotiocianatul de fenil).

3. Conclusions

The anils (V) and their derivatives (VI) and (VII) are obtained with good yields. Taking into account that the molecules of these compounds consist of various complexing groups, namely: $-OH$, $-NH_2$, $-C=N$, $-NHAC$, $-NHCNH$ — it is expected to be used like analytical reagents for many cations. Their good complexing properties correspond well to the unusually deshielding ($\delta = 10.12$ ppm) of OH proton.

STUDY ON THE INFLUENCE OF SOME PARAMETERS ON THE VINYL ACETATE POLYMERIZATION IN THE PRESENCE OF SEPHADEX G-50

BY

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1. Introduction

During the last years the matrix polymerization became the subject of many investigations.

The present data allow its defining as the reaction of forming macromolecular compounds on supports (matrices) which determine at least one of the properties of the final product [1]. In addition to the studies on the matrix polymerization process the characterization of the inclusion products, formed by the combination between the „host“ molecules (that is the molecules component of the matrix) and the „guest“ ones (the initial monomer and the resulted polymer molecules, respectively) was followed.

The ability of cyclodextrins to form inclusion compounds with various organic and anorganic substances [3] and the induced catalysis of certain reactions [4], [5] are explained by means of the known theory „lock“ and „key“ [2].

In the present paper the matrix photopolymerization of vinyl acetate (guest) in the presence of Sephadex gel (host) is studied, the influence of some factors on the polymerization being mainly investigated.

2. Experimental

2.1. Experiment Programme

For studying the matrix polymerization of vinyl acetate a mathematical model of the form given below was tried:

$$(1) \quad Y = b_0 + \sum_{i=1}^3 b_i x_i + \sum_{i \leq j}^4 b_{ij} x_i x_j,$$

where Y denotes the polymerization yield, x_i, x_j — reaction parameters, b_i, b_{ij} — regression coefficients.

To obtain the regression coefficients in Eq. [1] the method of „second order experiment programming“ was used [6], [7]. The experimental range and the codifications of variables are given in Table 1. In Table 2 the experimental data together with the calculated and found yield values are listed.

The data given in Table 2 allowed the calculation of the regression coefficients given in Table 3. The insignificant coefficient, according to the t test were eliminated.

Table 1
Codifications of the Variables for Experiment Programming

Real variable	Code				
	-1.682	-1	0	1	1.682
X_1 (T, °C)	-26.82°C	-20°C	-10°C	0°C	+6.82°C
X_2 (τ , h)	3.318	4	5	6	6.682
X_3 ($\frac{\text{Seph.}}{\text{V.A.}}$)	2.159	2.5	3	3.5	3.841

Table 2
Variation of the Polymerization Yield as a Function of Experimental Conditions

No.	X_1	X_2	X_3	X_1 (T, °C)	X_2 (τ , h)	X_3 ($\frac{\text{Seph.}}{\text{V.A.}}$)	Exp. %	Calc. %
1	-1	-1	-1	-20	4	2.5	1.5	1.63
2	1	-1	-1	0	4	2.5	51.40	50.60
3	-1	+1	-1	-20	6	2.5	7.38	6.65
4	1	+1	-1	0	6	2.5	60.5	59.6
5	-1	-1	1	-20	4	3.5	1.11	0.90
6	1	-1	1	0	4	3.5	31.3	30.99
7	-1	+1	1	-20	6	3.5	2.28	1.94
8	1	+1	1	0	6	3.5	37.25	36.02
9	-1.682	0	0	-26.82	5	3	2.69	2.94
10	+1.682	0	0	+6.82	5	3	71.21	72.78
11	0	-1.682	0	-10	3.318	3	8.98	9.23
12	0	+1.682	0	-10	6.682	3	16.26	17.67
13	0	0	-1.682	-10	5	2.159	31.09	31.99
14	0	0	+1.682	-10	5	3.841	10.75	11.54
15	0	0	0	-10	5	3	37.92	37.86
16	0	0	0	-10	5	3	37.86	37.86
17	0	0	0	-10	5	3	37.94	37.86
18	0	0	0	-10	5	3	37.75	37.86
19	0	0	0	-10	5	3	38.06	37.86
20	0	0	0	-10	5	3	37.98	37.86

2.2. Working Procedure

The vinyl acetate (V.A.) photopolymerization was carried one in inert medium, being initiated by the UV radiations obtained with help of a lamp with Hg vapours ($P=500$ W) and the influence of temperature, irradiation duration and reagent weight ratio on the polymerization yield followed.

The monomer freshly distilled was added to the Sephadex gel in aqueous medium (water to Sephadex weight ratio = 10/1). The polymer separation from support was carried out by dissolution in methanol, filtration and reprecipitation with excess water. The obtained product was purified by repeated precipitations and dried under vacuum at 30°C.

3. Results and Discussion

The experiments were aimed to settle the optimum reaction conditions by following the influence of different parameters (temperature, reaction time, Sephadex to V. A. weight ratio) on the process development.

The use of relation [1], for constant temperature ($x_1 = +70^\circ\text{C}$) allowed to follow the yield variation in time for various values of the reagent ratios (Sephadex to V. A.) (Fig. 1).

The highest yields are noticed for a reaction duration of 5 hours and Sephadex to V.A. ratios between 2.15 and 3. The theoretical results obtained for a constant reagent ratio (Sephadex/V.A. = 2.5, the optimum value according to Fig. 1, that is for $x_3 = \text{const.} = 2.5$) are represented in Fig. 2.

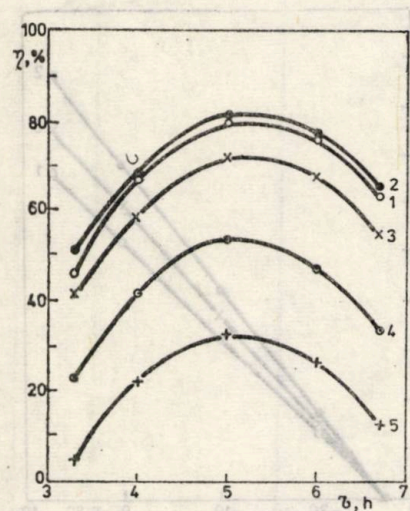


Fig. 1. — Yield variation versus time at constant temperature and different reagent ratios.

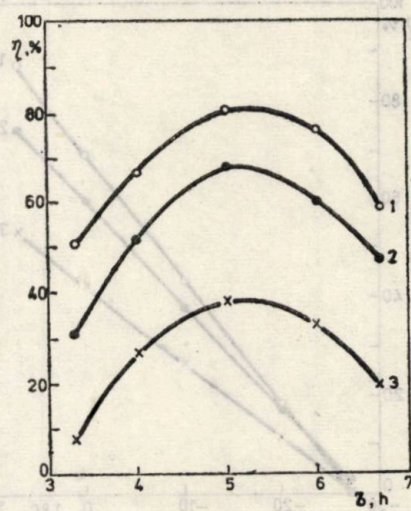


Fig. 2. — The temperature influence on the yield at constant reaction duration and reagent ratio.

Table 3

Values of the Regression Coefficients for the Object Function

Regression coefficient	Object function %
b_0	37.866
b_1	20.759
b_2	2.511
b_3	- 6.078
b_{11}	- 0.027
b_{22}	- 8.631
b_{33}	- 5.696
b_{12}	0.9975
b_{13}	- 4.728
b_{23}	- 0.9937

As can be seen in Fig. 2 the yield decreases in all cases with decreasing of temperature, attaining the maximum at reaction duration of 5 hours (82% at +7°C and 38% at -10°C, respectively).

The theoretical variation of the yield with Sephadex to V.A. ratio, at constant temperature ($x_1 = \text{const.}$) and various reaction durations

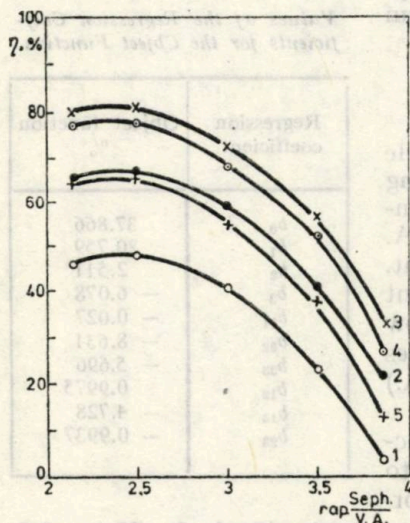


Fig. 3. — Yield variation with reagent ratio at constant temperature and various reaction durations.

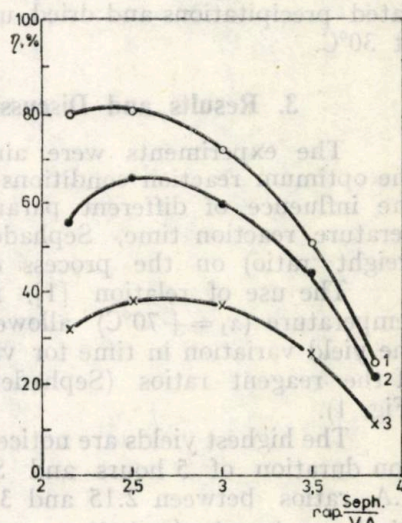


Fig. 4. — Temperature influence on the yield for various reagent ratios, at constant reaction durations.

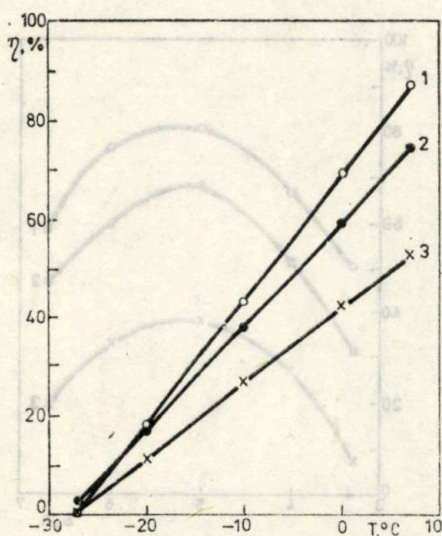


Fig. 5. — Influence of the reagent weight ratio on the yield variation with temperature for the same reaction duration.

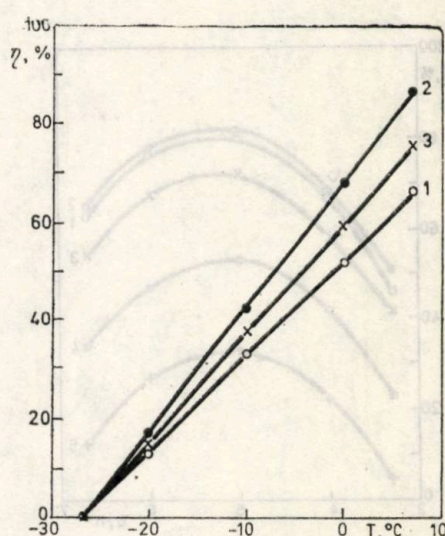


Fig. 6. — Influence of the reaction duration on the yield variation with temperature, at constant reagent ratio (2.5).

(Fig. 3) confirms the attaining of highest yields for 5 h duration and 2.5 reagent ratio.

As results from Fig. 4 the optimum temperature for the polymerization process is 6.82°C.

For the same reaction duration (5 hours, $x_2 = \text{const.}$) the yield increase with increasing temperature, the most significant variation being noticed for Sephadex to V.A. ratio of 2.5 (Fig. 5).

Similar conclusions regarding the optimum conditions of the polymerization (reaction duration 5 h, temperature 7°C, Sephadex/V.A. weight ratio=2.5) can be drawn by analysing the curves represented in Fig. 6.

4. Conclusions

The correlation of the theoretical results obtained by the method of second order factorial programming with the experimental data allowed to settle the optimum polymerization conditions for V.A. polymerization as follows: temperature $\sim 7^\circ\text{C}$, reaction duration 5 h, Seph./V.A. weight ratio = 2.5.

The excess Sephadex decrease the yield significantly. Temperatures above 0°C markedly increase the reaction rate which results in increasing yields up to 80%.

By comparing the results obtained in the presence or absence of Sephadex, respectively, the catalytic role of the latter is evidenced.

Further investigations are necessary to determine the polymer stereoregularities and to elucidate the Sephadex action as matrix.

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STUDIUL INFLUENȚEI PARAMETRILOR ASUPRA POLIMERIZĂRII ACETATULUI DE VINIL ÎN PREZENȚA DE SEPHADEX G-50

(Rezumat)

S-a studiat polimerizarea acetatului de vinil în prezență de Sephadex G-50 sub acțiunea radiațiilor UV.

Efectuarea unui studiu teoretic (programare factorială de ordinul II) precum și datele experimentale conduc la concluzia că temperatura, timpul de reacție și raportul gravimetric dintre Sephadex G-50 și acetatul de vinil în amestecul inițial, exercită o influență sensibilă asupra randamentului de polimerizare.

MECHANO-CHEMISCHE REAKTIONEN VON POLYVINYLCHLORID**5. VERÄNDERLICHKEIT DER FESTIGKEIT VON PVC-S DURCH MECHANO-ABBAU IM HETEROGENEN SYSTEM**

VON

CLEOPATRA VASILIU-OPREA und MARCEL POPA**1. Betrachtungen über das Bruchverhältnis von Polymeren und ihrer Festigkeit [1]...[20]**

Die Feststellung des Verhältnisses zwischen der Einwirkung äußerer Kräfte und der Reaktion eines Materials auf molekularer oder atomarer Ebene wie auch die Vorhersage seiner makroskopischen Eigenschaften auf Grund seiner Struktur ist ausserordentlich wichtig.

Das Reißen des Materials bei Anwendung äußerer Kräfte besteht in einer Aufspaltung von Bindungen, welche den Querschnitt durchqueren an welchem der Riß durchläuft. Die theoretische Festigkeit wird also von der Summe der zum Aufreißen der individuellen Bindungen nötigen Kräfte bestimmt sein. Die Festigkeitsberechnung beruht auf der Bestimmung der Anzahl und der Natur der spaltbaren Bindungen; diese geht von der bestimmten gegebenen Struktur des Materials und Kenntnis der Rißgeometrie aus. Gewöhnlich unterscheiden sich die für diese Stoffcharakteristik berechneten Werte von der experimentell gemessenen, da man bei der theoretischen Analyse von der Voraussetzung ausgeht, daß sich die im Körper beim Anlegen der Kraft entwickelte Spannung gleichförmig auf seine Bausteine verteilt.

Die im Vergleich mit der von der Theorie vorausgesagten niedrige tatsächliche Festigkeit der Körper erklärt sich aus der Unvollkommenheit ihres Aufbaues. Die baulichen Defekte — Verhagerungen, zwischen-kristalline Grenzen, Faser- und Globulärstruktur, amorphe Bereiche aus makromolekularen Verbindungen — schaffen die Bedingungen für das Auftreten von schwachen Punkten, sowie für die ungleichmässige Verteilung der mechanischen Energie.

Die strukturellen Defekte — sei es, daß sie im Material vorgebildet sind, daß sie sich während einer mechanischen Bearbeitung einstellen — bestimmen ihrerseits die örtliche Verteilung der Spannungen. In einem beliebigen isotropen Material geschieht der Aufriß durch das Anwachsen der größten Wirkung. Die Bestimmung des Spannungszustandes, der eben diesen Effekt verursacht, kann man auf zwei Wegen angreifen.

Die Gleichungen, welche die Spannungsverteilungen beschreiben, zeigen, daß die örtlichen Spannungen in der Nähe des Defektes um vieles größer sind als ihr Mittelwert im übrigen Körper, deshalb geschieht der örtliche Riß des Materials beim Anwachsen des größten Defektes. Dieser Effekt bedingt seinerseits das Ansteigen örtlicher Spannungen. So wird das System immer unbeständiger; es setzen sich in ihm die Aktivierung, Entwicklung und Fortpflanzung des Bruches fest.

Der Vorgang kann auch energetisch analysiert werden. In diesem Fall hängt das Reißkriterium von der Gesamtenergie des konservativen Systems ab, das sich im Masse der Vergrößerung der Ausmasse des Defektes verkleinert. Dieses Kriterium wird aus thermodynamischen Bedingungen abgeleitet. (Das System heißt konservativ, wenn unter der Einwirkung einer konstanten Kraft eine mechanische Arbeit durch Verlagerung seiner äußern Grenzen geleistet werden kann).

In der ersten Behandlungsweise wird eine besondere Bedeutung dem Punkte gewidmet, in welchem die Spannung ihren Höchstwert erreicht. Gewöhnlich nimmt man zum Modell ein kontinuierliches Medium und akzeptiert es, daß der Defekt als ein längliches Gebilde, Riß

genannt, erscheint, welches durch Dicke und einem Krümmungsradius Null gekennzeichnet ist. Die realen Systeme weisen aber einen bestimmten Wert des Krümmungsradius auf, wobei die Ausmasse des Risses von der Struktur des Materials bestimmt sind.

Im Falle der energetischen Behandlung wird das System als ein Ganzes aufgefaßt und dank dieses Umstandes treten keine Schwierigkeiten bei der Analyse des Auftretens eines linearen Risses auf.

Im Anfangsstadium ist also der Riß auf Mikrofragmente lokalisiert, die vom heterogenen Charakter des realen Körpers affektiert werden und führt schließlich zum Auftreten mikroskopischer Fissuren, welche die gleichen Ausmasse nach der Größenordnung wie die des defekten Bereiches aufweisen.

2. Abhängigkeit des mechanischen Verhaltens bei Zugbeanspruchung von PVC-S von der Natur der durch Mechano-Abbau gebildeten Oberflächen

2.1. Voraussetzungen der Untersuchung

Man geht von der Auffassung aus, die im § 1 dieser Arbeit behandelt wurde, daß nämlich die statistisch auf verschiedenen Höhenlagen der Struktur eines bestimmten Polymern, inbegriffen an der kompositionellen verteilten Defekte, die Verringerung der Festigkeit desselben verursachen; demgemäÙ formuliert man die Hypothese, daß durch Vereinheitlichung der Granularzusammensetzung von PVC-S man zur Verbesserung seiner Festigkeitswerte beitragen kann.

Um den Veränderungsbereich der Granulometrie von PVC-S zu verengern, verwendete man den milden Mechano-Abbau, durch Ultraschallung. Arbeitsverfahren und Analyse sind in unsern Arbeiten beschrieben [21]...[24].

2.2. Abhängigkeit des mechanischen Verhaltens bei Zugbeanspruchung von mechanisch unbearbeitetem PVC-S von seiner Granularzusammensetzung

Eine erste Reihe von Zugbeanspruchungen wurde zwecks Feststellung des Einflusses der Teilchenausmasse auf die physiko-mechanischer Kennwerte bei Polymern angestellt, die keine Einwirkung mechanischer Energie erfahren haben. Zu diesem Zweck unterwarf man der Ultraschallung ein in seiner Granularzusammensetzung polydisperses Polyvinylchlorid, dessen Oberflächeneigenschaften in einer früheren Arbeit [23] analysiert und besprochen worden sind. Man untersuchte das Verhalten bei diesem Prozeß von zwei Fraktionen: $\varnothing = 100 \mu\text{m}$, quantitativ im studierten Polymern vorherrschend, und $\varnothing = 45 \mu\text{m}$, aus feinen Partikeln bestehend.

Das Verhältnis zwischen den Oberflächen-Charakteristiken des durch Ultraschallung unbearbeiteten Ausgangspolymern, ausgedrückt im Teilchendurchmesser, ergibt sich aus Tabelle 1. Man stellt fest, daß die beste Reißfestigkeit einer Probe zukommt, deren Ausmasse einheitlich sind und welche die feinste Granulometrie ($\varnothing = 45 \mu\text{m}$) aufweist.

Die Ultraschallung erfolgte bei verschiedenen Zeitdauern in einem Intervall von 3 bis 20 Stunden und bedingte eine Veränderung der granular Zusammensetzung des Polymern, wie aus Abb. 1 hervorgeht. Die durch $\varnothing = 45 \mu\text{m}$ und $\varnothing = 100 \mu\text{m}$ charakterisierten Fraktionen, die durch

Sieben aus dem ultrabeschallten Polymeren angetrennt wurden, bildeten den eigentlichen Gegenstand der Untersuchung des mechanischen Verhaltens.

Tabelle 1

Physiko-mechanische Kennwerte von nicht ultrabeschalltem PVC

Nr.	Polymer	σ_r Kgf/cm ²	ε %
1	PVC, granulometrisch nichtfraktioniert $\varnothing = 200..45 \mu\text{E}$	183,66	509
2	$\varnothing = 100 \mu\text{m}$	186,92	498
3	$\varnothing = 45 \mu\text{m}$	193,24	504

Die Bildung neuer Oberflächen durch Mechano-Dispersion wurde auch direkt durch optische Mikroskopie festgestellt. Die Analysen bezogen sich auf einige durch Schwingmahlung und Ultrabeschallung bearbeiteten Proben: es wurde ein Apparat Typ MC-1 verwendet, der von IOR, Bukarest, geliefert worden war.

Die für das Studium bestimmten PVC-S-Proben wurde in ein Epoxydharz aus vier Komponenten (Monomer, Auslöser, Beschleuniger, Weichmacher) eingeschlossen und in den Trockenschrank bei 40°C, 48 Stunden zur Polymerisation eingeführt. Man wählte als Einschlußmedium Epoxydharz, da dieses einen scharf unterschiedlichen Brechungsindex gegenüber dem analysierten Probe aufweist und so eine deutliche Veranschaulichung des Probenquerschnittes im Einschlußmedium gestattet.

Die Blöcke mit den eingeschlossenen Proben wurden an einem Ultramikrotom bei einer Stärke von 1 μ sektioniert. Um einem guten Kontrast zwischen dem Querschnitt der Probe und dem Einschlußmedium zu erhalten wurde eine Immersion in Wasser unter dem Deckglas beim Mikroskop durchgeführt.

Eine erste Analysenprobe bildet die Fraktion $\varnothing = 80 \mu\text{m}$, aus welcher eine Einzelgranule gewählt wurde; diese ist auf Abb. 2 dargestellt, wo sie mit andern solchen Gebilden verglichen wird, die dem Produkt $\varnothing = 80 \mu\text{m}$ angehören und aus dem 40 Stunden lang ultrabeschallten, granulometrisch nichtsortiertem Polymeren abgetrennt wurden. Das erhaltene mikroskopische

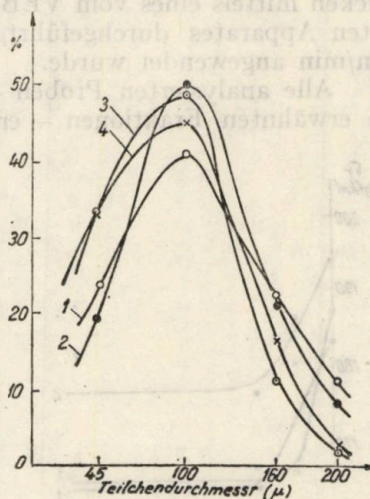


Abb. 1. — Granulometrische Verteilung von PVC-S bei Verwendung zur Bestimmung der Reißfestigkeit: 1 — Anfangswert; 2—3 Stunden ultrabeschallt; 3 — idem, 6 Stunden; 4 — idem, 20 Stunden.

sche Abb. 3 veranschaulicht die Erhöhung der Porosität des Materials, da der verdunkelte dem Granuliten entsprechende Teil an Intensität bedeuten abnimmt. Diese Folgerung stimmt auch gut mit den Ergebnissen überein, welche der Veränderung der Materialdichte durch mechanische Verarbeitung entsprechen [23].

Die Verarbeitung durch Schwingmahlung des ungesiebten Polymern die unter verschiedenen Bedingungen durchgeführt wurde, löst gleichfalls eine Reihe von Veränderungen aus, die durch mikroskopische Analyse feststellbar sind (Abb. 4...6). In diesem Fall geht dem Zerkleinerungsvorgang eine Zerdrückung der Granulen voraus (Abb. 4), die sich in einer Modifizierung der gesetzten und ungesetzten Dichten widerspiegelt [23]. Man stellt fest, daß die von der Einwirkung der Suspensionsflüssigkeit und der Temperatur ausgeübten Einflüsse für die Zerkleinerungsprozesse entscheidend sind (Abb. 5 und 6).

Die Natur der durch Mechano-Dispergierung neu gebildeten Oberflächen wurde mit dem durch die Reißfestigkeit ausgedrückten mechanischen Verhalten des Polymern verglichen.

Der erwähnte physiko-mechanische Kennwert wurde gemäß den geltenden Standards bestimmt, wobei Platten von 1 mm Stärke verwendet wurden. Die Zugspannungsproben wurden an Serien von je fünf Probestücken mittels eines vom VEB Thüringer Industriewerk Rauenstein gelieferten Apparates durchgeführt, wobei eine Ziehgeschwindigkeit von 300 mm/min angewendet wurde.

Alle analysierten Proben — sowohl das ungesiebte Polymer als auch die erwähnten Fraktionen — erwiesen für das Versuchs-Zeitintervall eine

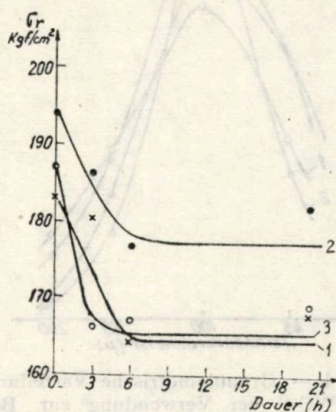


Abb. 7.—Veränderlichkeit der Reißfestigkeit σ_r , [Kg/cm²], mit der Dauer der Ultrabeschallung (Versuchskurven): 1—PVC-S, ungesiebt; 2 — $\varnothing = 45 \mu\text{m}$; 3 — $\varnothing = 100 \mu\text{m}$.

Verringerung der physikalisch-mechanischen Kennwerte gemäß einem jedem Produkt eigentümlichen Exponentialgesetz (Abb. 7). Aus der Analyse dieser Ergebnisse ergibt sich die Folgerung, daß σ_r den größten Wert bei der Fraktion mit dem Teilchendurchmesser $\varnothing = 45 \mu\text{m}$ aufweist; ist deutlich dem des Produktes mit $\varnothing = 100 \mu\text{m}$ und besonders dem des ungesiebten Produktes überlegen, welches das schwächste mechanische Verhalten zeigt. Die Veränderungen $\sigma_r = f(t)$ stimmen übrigens vollkommen mit den auf die granulometrische Verteilung bezüglichen Daten überein (Abb. 1).

Da die auf Abb. 7 dargestellten Veränderlichkeitskurven $\sigma_r = f(t)$ eine Verringerung dieser Größe gemäß einem Exponentialgesetz anzeigen, wobei das von J. S. U r z i m c w für die akustische Ermüdung polymerer Stoffe vorgeschlagene mathematische Modell [25] verwendet wurde, schritt man zur Aufstellung der Exponentialgleichung, welche die von der vom System absorbierten Energie abhängige, Variable korreliert, die vom Verfasser akustischer Parameter genannt wurde. Im

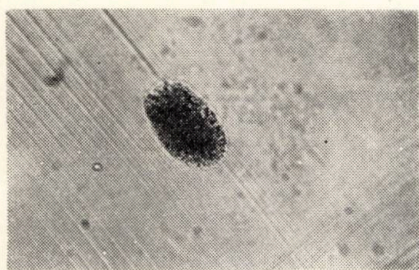


Abb. 2. — Ausgangs PVC - S,
 $\varnothing = 80 \mu\text{m}$.



Abb. 3. — 40 Stunden, als wässrige
Suspension ultraschalltes PVC - S.

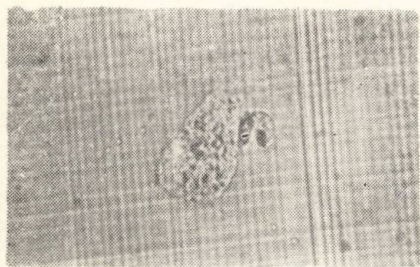


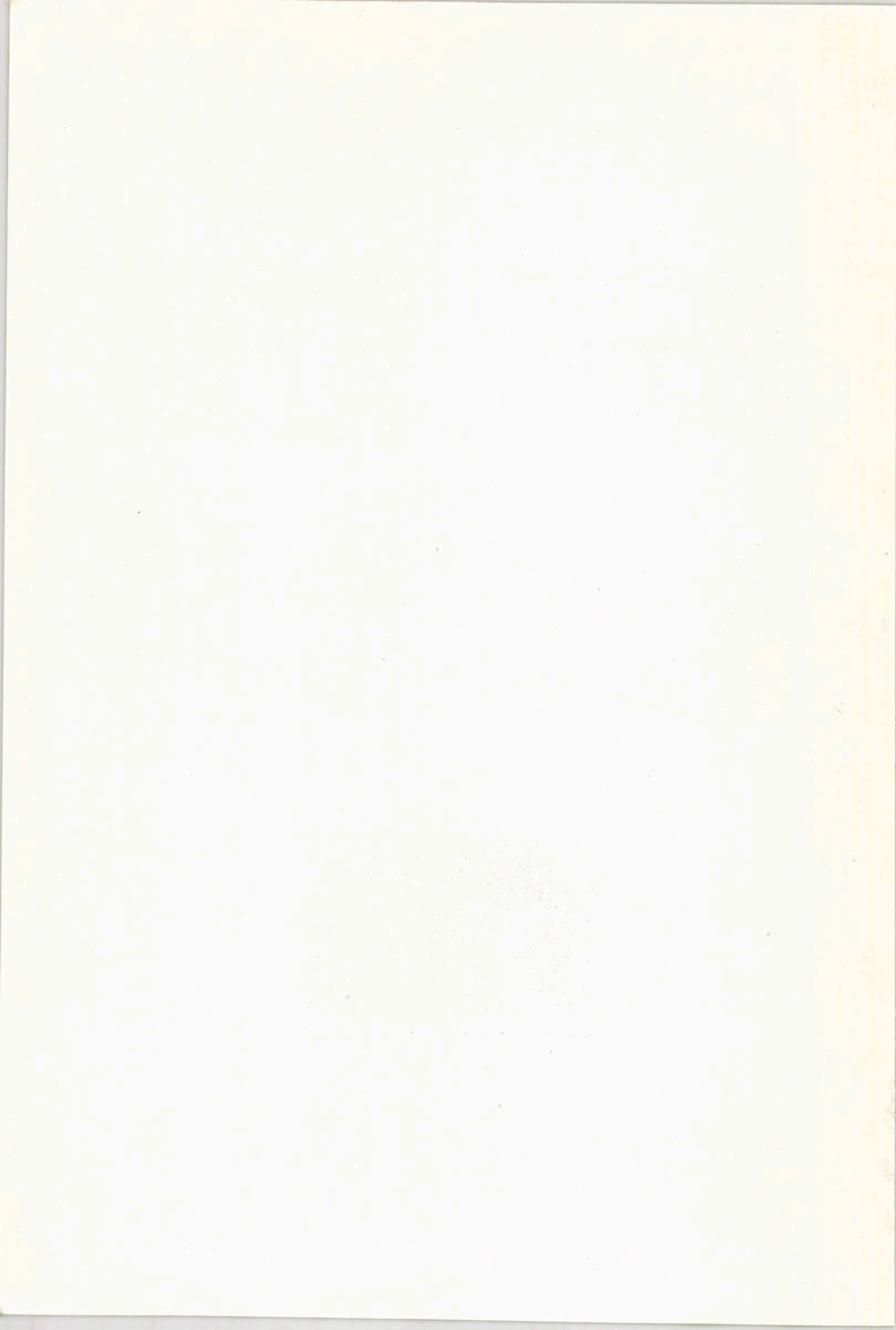
Abb. 4. — Ungesiebtes, als methanoli-
sche Suspension 1 Stunde lang bei Zim-
mertemperatur vermahlenes PVC - S.



Abb. 5. — Ungesiebtes, als methanolische
Suspension 1 Stunde lang bei -196°C
vermahlenes PVC-S.



Abb. 6. — Ungesiebtes, in Abwesenheit
von Methanol 1 Stunde lang bei -196°C
vermahlenes PVC-S.



vorliegenden Fall wird man die Veränderung der Reißfestigkeit σ_r mit der Dauer der Ultraschallung verfolgen.

Die vorgeschlagene Formel lautet:

$$(1) \quad \sigma_r(t) = \frac{\sigma_{r(cr)}}{1 + [\sigma_{r(cr)}/\sigma_{r(t)} - 1] e^{-\sigma_{r(cr)} K t}},$$

wobei: $\sigma_{r(t)}$ — Wert von σ_r in der Zeit t , $\sigma_{r(cr)}$ — kritischer Wert von σ_r , $\sigma_{r(t)}$ — Anfangswert (Höchstwert) von σ_r , K — Koeffizient dessen Bestwert aus den Versuchsergebnissen mittels der Methode der kleinsten Quadrate bestimmt:

$$(2) \quad K = \frac{\nu}{\sigma_{r(cr)}} \cdot \frac{\sum_i y_i N_i}{\sum_i N_i^2},$$

mit: ν — Frequenz des Ultraschallfeldes, N_i — Anzahl der Beanspruchungszyklen bei einer bestimmten Dauer,

$$(3) \quad y_i = \frac{\sigma_{r(cr)}/\sigma_{r(t)} - 1}{\sigma_{r(cr)}/\sigma_{r(t)} - 1},$$

worin n — Anzahl der Versuchsmessungen der laufenden Werte σ_r bei einer Zyklenzahl N_i .

Die zur Aufstellung der Formeln nötigen Angaben findet man in der Tabelle 2. Die Werte N_i wurden durch Vervielfachung der in Sekunden ausgedrückten Ultraschallungszeiten (die in den Versuchen angewendet wurden) mit der in Hertz ausgedrückten Frequenz des Ultraschallgenerators berechnet. Die erhaltenen Resultate sind in Tabelle 3 zusammengefasst.

Tabelle 2

Verhältnis verschiedener Fraktionen in mechanisch unverarbeiteten und in bei verschiedenen Zeitdauern ultraschallten PVC-S,

Probe	Fraktion, [%]				
	$\varnothing = 200$ μm	$\varnothing = 160$ μm	$\varnothing = 100$ μm	$\varnothing = 45$ μm	$\varnothing = 45$ μm
PVC-S, Ausgangsprodukt	11,41	22,05	41,20	21,35	4,13
PVC-S, 3 h ultraschallt	8,25	20,80	50,00	19,50	1,64
PVC-S, 6 h ultraschallt	2,14	11,10	49,20	33,70	4,10
PVC-S, 20 h ultraschallt	2,45	16,15	45,00	33,20	3,10

Auf grund des abgeleiteten theoretischen Modells wurden die Variationskurven σ_r — Dauer der Ultraschallung auf Abb. 8 dargestellt. Des weitem wurden die Variationsformeln von σ_r zur Überprüfung der Experimentellkurve benützt. In diesem Sinn wurden die σ_r -Werte für die Anfangs-

Tabelle 3
*Formulierung der Exponentialgleichung, die das mechanische Verhalten von PVC-S
 und seinen verschiedenen Fraktionen kennzeichnet*

Probe	Zeitdauer h	σ_r (cr) Kgf/cm ²	σ_r Kgf/cm ²	N_f Zyklen	y_f	K	Exponentialgleichung der Veränderlichkeit von σ_r
PVC-S Ø = 200... 40 µm	0	163,0	183,66	0	—	$1,8 \cdot 10^{-7}$	$\sigma_r(t) = \frac{163,00}{1 - 0,109 e^{-2,934 \cdot 10^{-5} t}}$
	3		181,38	$4,32 \cdot 10^8$	0,104		
	6		163,69	$8,64 \cdot 10^8$	3,328		
	20		168,06	$2,88 \cdot 10^9$	1,316		
PVC-S Ø = 45 µm	0	175,0	193,24	0	—	$1,2 \cdot 10^{-7}$	$\sigma_r(t) = \frac{175,00}{1 - 0,094 e^{-2,1 \cdot 10^{-5} t}}$
	3		185,59	$4,32 \cdot 10^8$	0,499		
	6		175,92	$8,64 \cdot 10^8$	2,930		
	20		182,78	$2,88 \cdot 10^9$	0,780		
PVC-S Ø = 100 µm	0	165,00	186,92	0	—	$2,1 \cdot 10^{-7}$	$\sigma_r(t) = \frac{165,0}{1 - 0,117 e^{-3,4 \cdot 10^{-5} t}}$
	3		165,68	$4,32 \cdot 10^8$	3,372		
	6		167,10	$8,64 \cdot 10^8$	2,194		
	20		168,74	$2,88 \cdot 10^9$	1,670		

proben und den der Dauer von 15 bzw. 20 Stunden entsprechenden, die nicht in die Berechnung der Koeffizienten y_i oder der Konstante K eingetreten sind, umgerechnet. Die durch Rechnen und experimentell erhaltenen Vergleichswerte sind in Tabelle 4 wiedergegeben. Man stellt

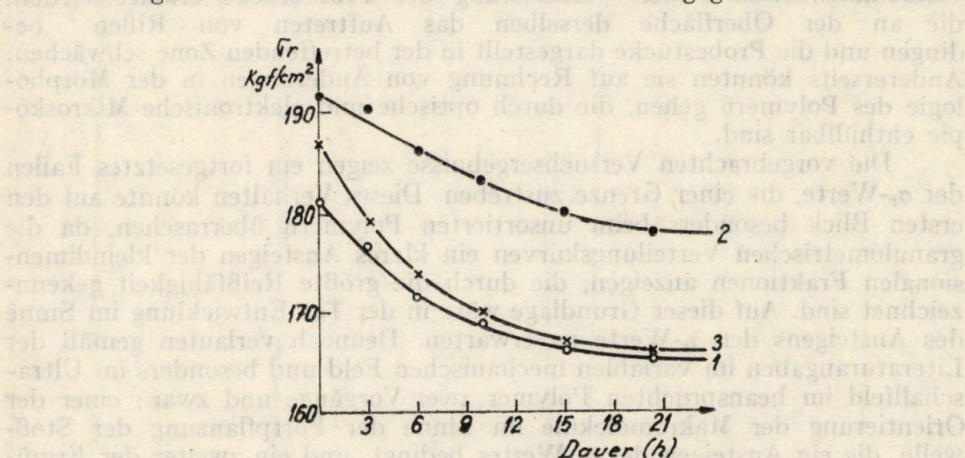


Abb. 8. — Theoretische Kurven der Veränderlichkeit von σ_r , [Kg/cm²], mit der Dauer der Ultraschallung: 1 — ungesiebtes PVC-S; 2 — PVC, $\emptyset = 45 \mu\text{m}$; 3 — $\emptyset = 100 \mu\text{m}$.

fest, daß die auf Grund des vorgeschlagenen Modells berechneten Werte und die experimentell gefundenen im Falle des Polymern, der keine mechanische Beanspruchung erfahren hat praktisch identisch

Tabelle 4

Theoretisch und experimentell abgeleitete σ_r -Werte.

Probe	Zeitdauer h	σ_r	
		berechnet	experimentell
PVC-S ungesiebt	0	182,90	183,66
	10	169,44	—
	15	166,67	—
PVC-S $\emptyset = 45 \mu\text{m}$	0	193,10	193,24
	10	183,05	—
	15	180,41	—
PVC-S $\emptyset = 100 \mu\text{m}$	0	186,90	186,92
	10	170,80	—
	15	167,00	—

sind; die den 10 bzw. 15 Stunden ultrabeschallten Proben angehörenden sind zufriedenstellend in der Experimentell-Variationskurve des akustischen Parameters (σ_r) eingeschrieben. Man kann demgemäß folgern, daß

das gewählte Modell gut mit dem Variationsgesetz der Reißfestigkeit im Ultraschallfeld übereinstimmt. Die Abweichungen, die gegenüber dem theoretischen Modell verzeichnet werden, können teils durch technische Unvollkommenheiten beider Vorbereitung der Probestücke erklärt werden, die an der Oberfläche derselben das Auftreten von Rissen bedingen und die Probestücke dargestellt in der betreffenden Zone schwächen. Andererseits könnten sie auf Rechnung von Änderungen in der Morphologie des Polymern gehen, die durch optische und elektronische Mikroskopie enthüllbar sind.

Die vorgebrachten Versuchsergebnisse zeigen ein fortgesetztes Fallen der σ_r -Werte, die einer Grenze zustreben. Dieses Verhalten könnte auf den ersten Blick besonders beim unsortierten Polymern überraschen, da die granulometrischen Verteilungskurven ein klares Ansteigen der kleindimensionalen Fraktionen anzeigen, die durch die größte Reißfähigkeit gekennzeichnet sind. Auf dieser Grundlage wäre in der Tat Entwicklung im Sinne des Ansteigens der σ_r -Werte zu erwarten. Dennoch verlaufen gemäß der Literaturangaben im variablen mechanischen Feld und besonders im Ultraschallfeld im beanspruchten Polymer zwei Vorgänge und zwar: einer der Orientierung der Makromoleküle im Sinne der Fortpflanzung der Stoßwelle, die ein Ansteigen des σ_r -Wertes bedingt, und ein zweiter der Ermüdung, da im Ultraschallfeld das Polymer wechselnden Belastungen und Erschlaffungen unterworfen ist, die mit sehr hoher Frequenz ablaufen.

Die Verringerung der Zugfestigkeit unter den beschriebenen Versuchsbedingungen, die akustische Ermüdung des Polymern, erklärt sich aber vor allem durch die Uneinheitlichkeit des der Verarbeitung unterworfenen Produktes, da die zwei analysierten Fraktionen vom Gesichtspunkte des mechanischen Verhaltens aus nach Durchführung der Ultraschallbehandlung getrennt wurden.

Da man an einer Probe erhöhter Homogenität ($\varnothing = 80 \mu\text{m}$) experimentierte, beobachtete man, daß im untersuchten Zeitabschnitt (15 min... 20 Stunden), σ_r sich praktisch nicht verändert, sondern Werte verzeichnet die denen des Ausgangsproduktes nahekommen (Tabelle 5). Die kann gut mit der granulometrischen Verteilung dieser Fraktion korreliert werden, die in diesem Intervall keinen quantitativ bedeutenden Übergang der studierten Fraktion in eine andere feinere aufweist, die sich gemäses der

Tabelle 5

Veränderlichkeit von σ_r mit der Dauer der Ultraschallung im Falle der Fraktion von $\varnothing = 80 \mu\text{m}^*$

	Dauer der Ultraschallung, [h]									
	0	0,25	0,5	1	1,5	2,5	5	10	15	21
σ_r , [Kgf/cm ²]	199,5	207,5	197,5	204,0	208,0	205,5	211	195,5	211,5	203

*) Bei der Vorbereitung der Prüflinge verwendete man Dioktyladipat als Weichmacher, während für den Rest der Prüflinge Dioktylphtalat verwendet wurde.

von uns erhaltenen Ergebnisse widerstandsfähiger erweist. Dagegen erfährt das durch den Teilchendurchmesser $\varnothing = 80 \mu\text{m}$ gekennzeichnete Produkt durch Ultraschallung eine neue Nichtvereinheitlichung dahin, daß in ihm neue Fraktionen mit $\varnothing \geq 80 \mu\text{m}$ auftreten. Man beobachtet, daß bei allen Zeitdauer die Fraktion mit $\varnothing = 80 \mu\text{m}$ quantitativ abnimmt, dennoch aber vorherrschend bleibt. Bedeutende Schwankungen des σ_r -Wertes dieser bei verschiedenen Zeiten ultraschallten Fraktion stimmen vollständig mit seinen granulometrischen Kennwerten überein [23]

Tabelle 6

Veränderlichkeit von σ_r mit der Dauer der Ultraschallung bei ungesiebteten PVC-S und der Fraktion von $\varnothing = 80 \mu\text{m}$, die nach der Mechano-Dispergierung abgetrennt wurde)*

Probe	Dauer der Ultraschallung, [h]			
	0	30	40	60
PVC-S ungesiebt	199,0	209,0	202,5	216,5
PVC-S, $\varnothing = 80 \mu\text{m}$	199,5	208,3	204,3	217,0

*) Bei der Vorbereitung der Prüflinge verwendete man Dioktyladipat als Weichmacher, während für den Rest der Prüflinge Dioktylphtalat verwendet wurde.

Unterwirft man ungesiebtetes Polymer einer bis auf 60 Stunden verlängerten Ultraschallungsbehandlung, so verzeichnet man nach der granulometrischen Fraktionierung eine ausgeprägte Verteilungsverengung [23] die ein Ansteigen der Reißfestigkeit sowohl beim unsortierten Polymer als auch bei der durch $\varnothing = 80 \mu\text{m}$ gekennzeichneten Fraktion zur Folge hat, die nach Ultraschallung quantitativ wächst (Tabelle 6).

Der Einfluß der granulometrischen Uneinheitlichkeit auf die Reißfestigkeit ist auch nach Ultraschallen des Polymer in Suspensionsform in wäßriger Lösung von 0,1% Natriummersolat augenscheinlich. Im Abb. 9 sieht man, daß das hinsichtlich der granulometrischen Zusammensetzung uneinheitliche Polymer durch die geringste mechanische Festigkeit (Kurve 7) gekennzeichnet ist. Das Ultraschallen begünstigt die Verbesserung dieser Eigenschaft, so daß fortschreitend bis zum Erreichen eines Grenzwertes der Aufenthaltsdauer im mechanischen Kraftfeld man eine Festigkeitserhöhung des Materials erhält. Der günstige Einfluß der Homogenität desselben geht auch daraus hervor, daß die Fraktionen von $\varnothing = 80 \mu\text{m}$ und $40 \mu\text{m}$ sich bei höhern Werten gegenüber dem uneinheitlichen Polymer einordnen (Kurven 2 und 3 gegenüber 7). Die im Abb. 9 dargestellten Kurven können in mehrere Fragmente zerlegt werden, wie folgt: die Abschnitte AB beschreibt die Veränderung der Reißfestigkeit in der ersten Zeitpunkten der Ultraschallung, wobei sie eine Verringerung dieses Kennwertes anzeigen, die umso ausgeprägter ist, je uneinheitlicher das der Verarbeitung unterzogene Ausgangsmaterial vom granulometrischen Standpunkt ist. Die Abschnitte BC, welcher das Zeitintervall von 10 bis 20 Stunden

definiert, weist in allen Fällen ein stufenweises Ansteigen von σ_r auf, das sich durch die Vereinheitlichung des Aufbaus sowohl auf granularer als auch auf molekularer Höhe erklären läßt (Ausrichtung der Makromoleküle in Richtung der Stoßwellenwirkung, Verengung des Variationsbereiches

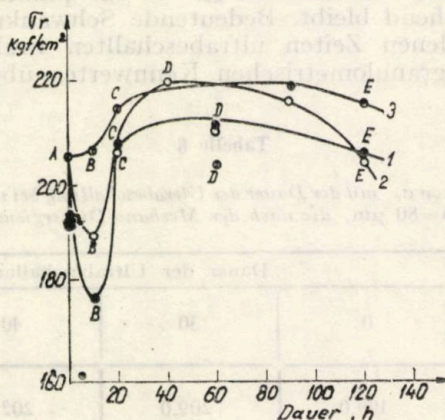


Abb. 9. — Veränderlichkeit der Reißfestigkeit σ_r , [Kgf/m²], mit der Dauer der Ultrabeschallung: 1 — ungesiebt ultrabeschalltes PVC-S (ultrabeschallt als Suspension in einer Lösung von 0,1% Mersolat); 2 — $\varnothing = 80 \mu\text{m}$, aus dem ungesiebt ultrabeschalltet Polymer abgetrennt; 3 — idem, $\varnothing = 40 \mu\text{m}$.

des Molekulargewichtes wegen des Aufreißen der Ketten, die eine gewisse Länge überschreiten).

Die Abschnitte CD entsprechen einer Vereinheitlichung der Granular-Zusammensetzung, welche gerade in diesem Bereich ein Optimum erreicht (notwendige Höchstdauer = 60 Stunden gemäß der granulometrischen Verteilungskurven) und in diesem Intervall eine Stabilisierung der Reißfestigkeit sichert. Es ist zu erwarten, daß sich in diesem Bereiche eine Ausrichtung der Makromoleküle einstellt, die eigentlich das Ansteigen der Festigkeit verursacht.

Die Abschnitte DE bedeuten eine Verringerung der Reißfestigkeit bei den drei untersuchten Proben, was von der starken Auflockerung der Granularstruktur und der einer Ermüdung des Polymeren entsprechenden Intensivierung des mechanochemischen Abbaus verursacht ist.

3. Diskussion und Interpretation der Ergebnisse

Die aufgeworfene Hypothese — die eine Möglichkeit des Ansteigens der Festigkeit bei Vereinheitlichung des Aufbaus auf allen Höhenlagen durch Beseitigung der Defekte von sich erscheint durch die Aufdeckung des Verhältnisses zwischen Granular-Zusammensetzung, Molekulargewicht und einem Kriterium der mechanischen Festigkeit — der Reißfestigkeit — gerechtfertigt.

Das wichtigste Ergebnis der vorliegenden Arbeit besteht in der Möglichkeit, das Polymer durch die Isolierung der Fraktion mit der feinsten Granulometrie zu fraktionieren, welche die höchste Reißfestigkeit aufweist.

Das Verhältnis zwischen der Granulometrie und den spätern Verwendungsmöglichkeiten des Polymern ergab sich aus dem Studium des Verhaltens des Polymern beim Quellen [24] und Reißen.

Geht man von der Annahme aus, daß das Polymer nach der Synthese der mechanischen Verarbeitung in Gegenwart verschiedener Ingredienzien zwecks Herstellung von Endprodukten bestimmt ist, so ergibt sich, daß seine granulometrische Uneinheitlichkeit im besprochenen Sinn die Eigenschaften des Endgemisches bedingen wird. Es ergab sich, daß bei Verwendung desselben Standard-Rezeptes, jedoch von Polymeren verschiedener Granulometrie, die Eigenschaften der Gemische nach ihrer Homogenisierung und also auch die der Endprodukte verschiedenartig sein werden; sie werden von diesem Faktor abhängen und geregelt werden, wie auch das ganze Verhalten des Materials unter Betriebsbedingungen. Es ergibt sich demgemäß die Wichtigkeit des Auffindens von Bedingungen und Methoden, Rahmen derselben Charge und mehr noch von Charge zu Charge ersichtlich ist.

Gemäß der in der vorliegenden und besonders in frühern Arbeiten [21]...[24] erhaltenen Daten kann behaupten, daß die Verbesserung dieser Eigenschaften durch eine mässige Mechano-Dispersierung des Polymern nach der Synthese geschehen kann. Ausserdem können durch das eingehende Studium der Mechano-Dispergierung und ihrem Verhältnis zum Mechano-Abbau wichtige Aufschlüsse auch für den Vorgang der Synthese selbst erhalten werden.

Wir sind der Ansicht, daß man die Hypothese der Abhängigkeit der Granular-Zusammensetzung des Polymern von den Ausmassen der in der Reaktionsmasse suspendierten Monomertropfen aufstellen kann. Die Bedeutung des Rührens für die Technologie der Suspensionspolymerisation ist bekannt. Man weiß, daß das Rühren nicht einförmig in der ganzen Reaktionsmasse ist, daß es eine parabolische Verteilung aufweist. Diese Eigentümlichkeiten haben zwei wichtige Folgen: a) die Monomerentropfen sind nicht dimensionseinheitlich im ganzen Reaktor; b) die Reaktionstemperatur ist nicht vollkommen einheitlich in der ganzen Reaktionsmasse.

Aus diesen Gründen wird die Güte des Polymern, welches in der Masse des Monomerentropfens nach bekanntem Mechanismus wächst, von den Bedingungen des Durchrührens abhängen. Mit der allergrößten Wahrscheinlichkeit übernimmt die Polymerisation in Suspension im Masse des Anwachsens der Monomerentropfen immer mehr die Charakteristiken und die Nachteile der Polymerisation in Masse. Die Optimisierung der granulometrischen Ausmasse und damit der Ausmasse der Monomerentropfen in der Reaktionsmasse wird also die Bildung eines Polymern von höhern Eigenschaften anregen.

Die in der vorliegenden und andern Arbeiten [21]...[24] erhaltenen Versuchswerte bilden einen Anfang und durch Vertiefung, Erweiterung und späteren Vervollständigung werden die Mittel gefunden werden die Verwendungseigenschaften des Polymern anzuregen, ihm eine bessere Qualität zu verleihen.

Im gegenwärtigen Stadium unserer Untersuchungen kann der Schluß gezogen werden, daß die Eigenschaften der Polyvinylchlorid-Suspension von ihrem chemischen Aufbau, der übermolekularen Struktur, der Granular-Zusammensetzung abhängen, die sich gegenseitig in ihren Auswirkungen durchdringen. Dieses Verhältnis kann verändert, es kann in die gewünschte Richtung durch mechanische Bearbeitung gelenkt werden, wobei ein adequates Arbeitsregime gesichert wird. Durch gelenkten Mechano-Abbau der Verbindung kann das Bruchphänomen geregelt werden, welches eigentlich die Oberflächeneigenschaften des verarbeiteten Polymern sichert.

Es wurde bewiesen, daß zwischen den molekularen und den makroskopischen Erscheinungen eine innige Beziehung besteht, die von der Natur des makromolekularen Stoffes, vom Medium, in welchen die Bearbeitung vor sich geht, von der Form in welcher die mechanische Energie übertragen wird abhängt.

4. Schlussfolgerungen

1. Das durch Polymerisations-Technologie synthetisierte Polyvinylchlorid in Suspension fällt granulometrisch uneinheitlich an; dies bedingt die Uneinheitlichkeit seiner Eigenschaften.

2. Fraktionen von feinsten Granulometrie sind durch die größte Reißfestigkeit charakterisiert.

3. Mässiger Mechano-Abbau durch Ultraschallung kann eine Möglichkeit der Vereinheitlichung der Granular-Zusammensetzung des Polymern bilden.

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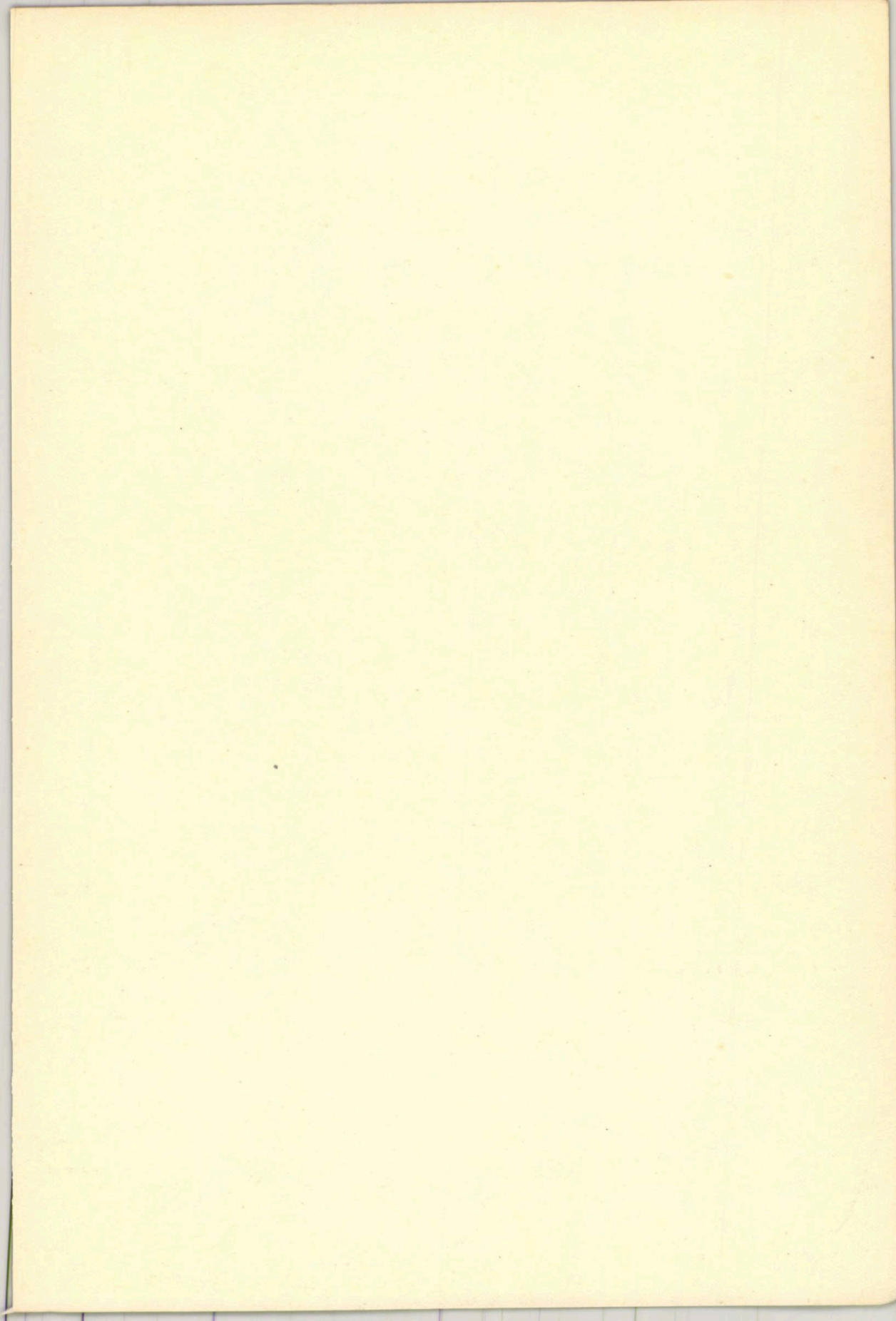
REAȚII MECANO-CHIMICE ALE POLI(CLORURII DE VINIL)

5. Modificarea rezistenței PVC-S prin mecano-degradare în sistem heterogen

(Rezumat)

Se corelează compoziția granulară a poli(clorurii de vinil)-suspensie cu comportarea sa mecanică (pentru care s-a luat drept criteriu rezistența la rupere, σ_r) și se propune ameliorarea acesteia prin solicitarea acustică a polimerului. Ultrasonarea îndelungată cu vibrații caracterizate prin frecvență joasă (40 kHz) poate fi definită ca un proces de obosire acustică, descris printr-o ecuația exponențială.





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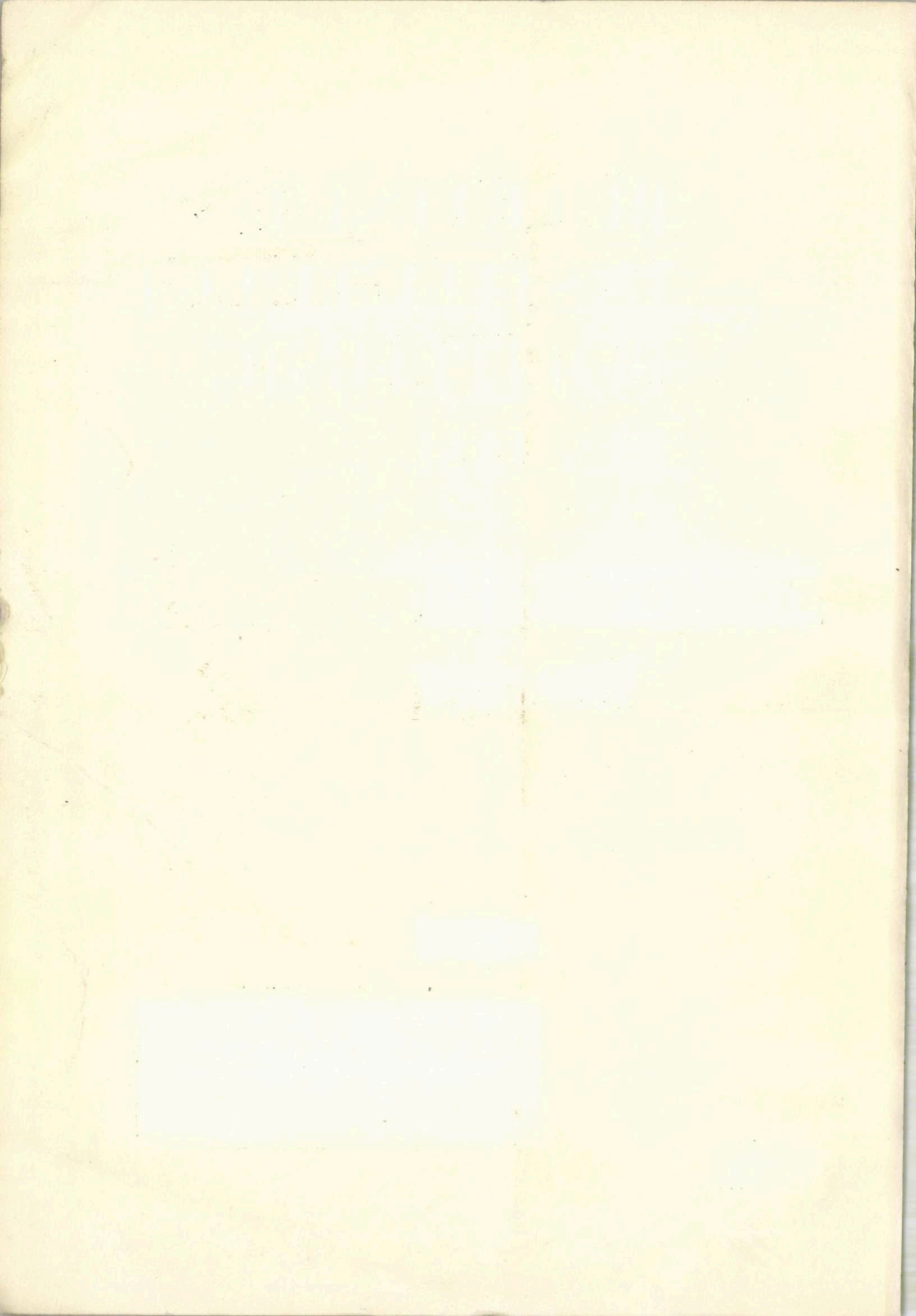
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L'ÉCHANGE IONIQUE DANS LE SYSTÈME Na_2WO_4 (EN SOLUTION) — AMBERLITHE IR 120(H^+)

I. L'ACIDE MÉTAWOLFRAMIQUE

PAR

CLEOPATRA CALU et N. CALU

1. Introduction

L'échange ionique dans les systèmes à W(VI) et des résines ioniques a été étudié par plusieurs chercheurs parmi lesquels [1]...[3]. Il a été réalisé en milieu acide (en solutions chlorhydriques et autres), où W(VI) passe sous forme de cations, quelquefois complexes.

À des faibles concentrations d'acide, l'acide wolframique précipite, ce, qui complique l'échange ionique [1].

Dans ce qui suit on présente les résultats d'une étude qui prouve la possibilité de l'échange ionique dans les solutions de wolframates; on met en évidence les espèces polywolframiques qui en résultent. Cette étude présente un réel intérêt pour la synthèse des acides polywolframiques tels que l'acide métawolframique, $\text{H}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]_{\text{aq}}$.

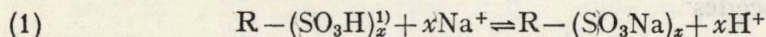
2. Résultats et discussions

2.1. Échange ionique dans le système Na_2WO_4 (en solution) — Amberlithe IR 120 (H^+)

Dans le système ci-dessus un échange ionique normal peut avoir lieu à des valeurs du $\text{pH} \approx 1$ ou plus élevées, comme il ressort des données fournies par ce travail, à savoir:

- a) l'échange a lieu selon la méthode statique, lorsqu'on ajoute la résine en petites quantités à une solution aqueuse de Na_2WO_4 ;
- b) le système hétérogène cationit — solution est agité sans cesse;
- c) l'échange peut avoir lieu à des températures comprises entre 0° et $\sim 100^\circ$, C sans que la capacité d'échange de la résine soit affectée.

L'échange ionique a lieu conformément à l'équation:



et la vitesse de réaction est considérable. Cet échange peut se dérouler dans le sens de la consommation des ions Na^+ , jusqu'au $\text{pH} = 1,5$.

L'évolution progressive du pH du système Na_2WO_4 (en solution) — Amberlithe IR 120(H^+) en ajoutant la résine est semblable à celle du sys-

¹⁾ On note avec $\text{R}-(\text{SO}_3\text{H})_x$ la résine Amberlithe IR 120 (H^+).

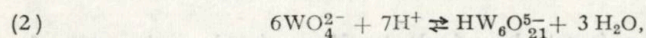
tème $\text{Na}_2\text{WO}_4\text{--HCl}$. Les ions H^+ provenus de l'échange ionique donnent avec les ions WO_4^{2-} des sels et des acides polywolframiques tout comme les acides minéraux forts (HNO_3 , HCl , etc.).

En plus, l'emploi de la résine présente l'avantage de produire des solutions à composés polywolframiques purs. Un excès de résine, dans la stœchiométrie globale de la réaction, ne modifie pas la concentration en protons de la solution, ce qui n'arrive pas dans le cas des acides forts.

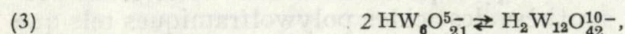
2.2. Quelques combinaisons polywolframiques résultées par l'échange ionique dans le système Na_2WO_4 (en solution) — Amberlithe IR 120 (H^+)

En général, en acidulant les solutions de wolframates, il se forme, en fonction du pH et de la concentration de la solution, une série de sels et d'acides polywolframiques. Ces espèces polywolframiques obtenues en première phase, passent avec le temps (en quelques dizaines de jours ou plus vite en les chauffant) dans des combinaisons plus stables. La stabilisation de ces solutions qui contiennent des combinaisons polywolframiques constitue une deuxième phase, où en dehors du pH et de la concentration de la solution, d'autres paramètres tels que le temps et la température jouent un rôle important [4] ... [27].

Ainsi, pour un pH ≈ 6 ou plus bas l'ion WO_4^{2-} se transforme en ion parawolframique A :

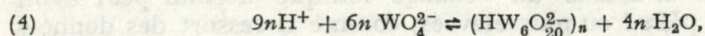


dont la structure est moins bien connue et qu'on n'a pu isoler à l'état cristallin. Celui-ci se transforme ensuite, lentement, en ion parawolframique B(Z) :



moins réactif, qui se sépare de la solution sous forme de cristaux, par exemple de $\text{Na}_{10}\text{H}_2\text{W}_{12}\text{O}_{42} \cdot 27\text{H}_2\text{O}$.

À un pH ≈ 5 ou plus bas, les parawolframates se transforment en ψ -métawolframates, $(\text{HW}_6\text{O}_{20}^{3-})_n$, dont la structure est, de même, peu connue. Ceux-ci se transforment lentement en métawolframates ($\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$):



Il est possible que d'autres espèces tels que les polywolframates X, Y, etc. prennent naissance en même temps, [13], [27].

On a étudié les combinaisons polywolframiques résultées par échange ionique, par la méthode spectrophotométrique, par des mesures du pH et par d'autres procédés.

2.3. Déterminations spectrophotométriques

Les acides polywolframiques résultés par échange ionique ont été étudiés par voie spectrophotométrique, par rapport aux données obtenues avec des solutions standard et aussi aux données de la littérature [13].

On a préparé les solutions standard d'acide métawolframique par les méthodes classiques [28], [29] et on a effectué ensuite l'analyse spectrophotométrique en vérifiant les lois générales de l'absorption (Fig. 1).

Il résulte, de cette analyse que la bande d'absorption à $\lambda_{\max} = 258$ nm et $\epsilon_{\max} = 3,85 \cdot 10^4$ l. mol⁻¹ (en polyacide) est caractéristique pour l'acide métawolframique.

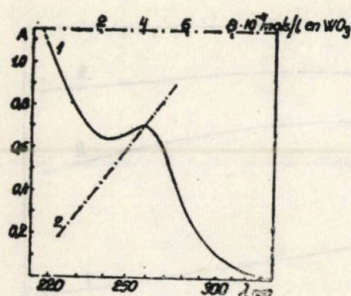


Fig. 1. — 1 — Spectre d'absorption en UV d'une solution d'acide métawolframique; $C_{\text{WO}_3} = 4,0 \cdot 10^{-4}$ mols/l²; 2 — Vérification de la loi de Lambert-Beer pour $\lambda_{\max} = 258$ nm; cuve 0,5 cm.

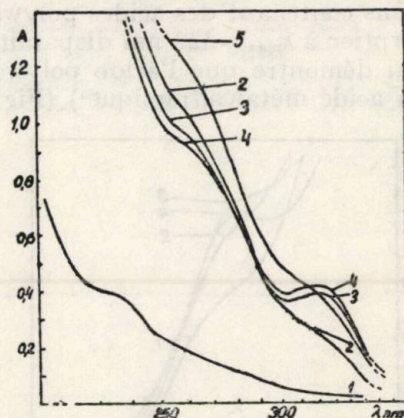


Fig. 2. — Spectres d'absorption en UV enregistrés pour des solutions fraîches d'acides polywolframiques (obtenues par échange ionique intégral), à la température ordinaire; $C_{\text{WO}_3} = 1 \cdot 10^{-4}$ (1); $1 \cdot 10^{-3}$ (2); $1 \cdot 10^{-2}$ (3); $1 \cdot 10^{-1}$ (4) et 1 mols/l (5); cuve = 1 cm.

Dans le système ci-dessous, l'échange ionique peut être intégral ou partiel. Pour la même concentration en Na_2WO_4 on peut obtenir un pH plus ou moins grand, avec des implications sur les espèces polywolframiques résultées.

a) Échange ionique intégral

D'abord on a suivi l'échange ionique sur des solutions de concentrations en Na_2WO_4 variant entre 1 et $1 \cdot 10^{-4}$ mols/l. Pour le réaliser intégralement on a pris la résine en excès, en opérant ainsi à un pH assez bas, $\text{pH} \approx 2$ (Fig. 2).

De l'étude de cet échange ionique (intégral) on constate que :

a) la bande d'absorption à $\lambda_{\max} = 258$ nm est peu contourée dans les solutions fraîches d'acides polywolframiques, ce qui prouve l'absence de l'acide métawolframique ;

b) dans ces solutions, de concentrations variant entre $1 \cdot 10^{-1}$ et $1 \cdot 10^{-2}$ mols/l Na_2WO_4 (et même en dehors de ces limites) et de $\text{pH} = 2 \dots 3$, une

²) On exprime la concentration des solutions de sels et d'acides polywolframiques (respectivement) en mols/l WO_3 .

³) Les concentrations mentionnées sont celles auxquelles l'échange ionique a eu lieu. Pour les mesures spectrophotométriques on a dilué les solutions à $1 \dots 4 \cdot 10^{-4}$ mols/l WO_3 . Les bandes d'absorption se modifient dans le temps comme suite des transformations subies par les espèces polywolframiques.

bande d'absorption à $\lambda_{\max}=322$ nm fait son apparition que l'on attribue à une espèce que les auteurs ont nommé *acide polywolframique T* (transitoire).

L'espèce *T* ressemble au polywolframate *Y* signalé dans les travaux [13], [27], mais sa masse ionique est beaucoup plus grande [30].

Par stabilisation dans un intervalle de temps de 30 à 40 jours, les solutions contenant des acides polywolframiques se modifient. La bande d'absorption à $\lambda_{\max}=322$ nm disparaît et celle à $\lambda_{\max}=258$ nm se développe, ce qui démontre que l'acide polywolframique *T* et d'autres encore passent en *acide métawolframique*⁴⁾ (Fig. 3 et 4).

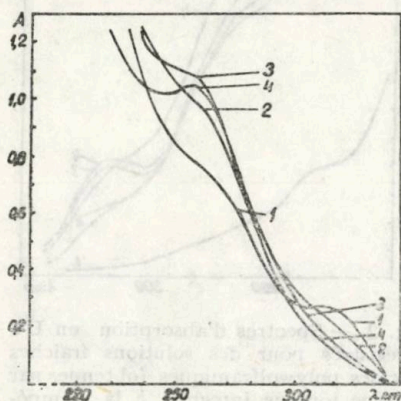


Fig. 3. — Spectres d'absorptions en UV enregistrés dans une solution d'acides polywolframiques (obtenus par échange ionique intégral) pendant les divers stades de vieillissement, respectivement de stabilisation des processus, à la température ordinaire; 1 — solution fraîchement préparée; 2 — solution à 5 jours; 3 — solution à 25 jours; 4 — solution à 50 jours depuis la préparation; $C_{\text{WO}_3}^{(3)} = 6 \cdot 10^{-2}$ mols/l; pH = 2,4; cuve = 1 cm.

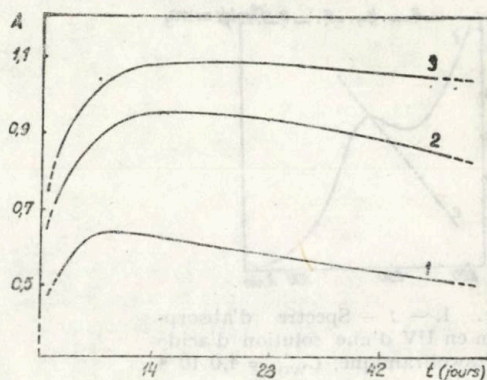


Fig. 4. — Courbes $A = f(t)$ de quelques solutions contenant des acides polywolframiques (obtenus par échange ionique intégral), pour $\lambda_{\max} = 258$ nm: 1 — $C_{\text{WO}_3}^{(3)} = 4 \cdot 10^{-2}$ mols/l; pH = 2,6; 2 — $C_{\text{WO}_3}^{(3)} = 6 \cdot 10^{-2}$ mols/l; pH = 2,4; 3 — $C_{\text{WO}_3}^{(3)} = 8 \cdot 10^{-2}$ mols/l; pH = 2,7; cuve: 1 cm.

À chaud, la stabilisation des solutions d'acides polywolframiques découle beaucoup plus vite, en approximativement 5 h, à 95°...98°C.

b) Échange ionique partiel

Dans la synthèse de l'acide métawolframique ou de son sel métallique, l'échange ionique partiel présente aussi une certaine importance. Celui-ci se déroule en présence d'une quantité de résine moindre que celle indiquée par la stœchiométrie de la réaction globale, en assurant, à la fois, le maintien de la solution à des valeurs du pH plus élevées, par exemple de 3,6 et 5,4 (Fig. 5 et 6).

⁴⁾ Après 10...20 jours, en vieillissant, dans les solutions d'acides polywolframiques, de petites quantités d'acide wolframique précipitent — phénomène commun aux solutions de ces polyacides.

Pour cet échange ionique (partiel), on peut faire les constatations suivantes :

a) dans les solutions fraîches de sels et d'acides polywolframiques de $\text{pH}=3,6$ et $5,4$, la bande d'absorption à $\lambda_{\text{max}}=322$ nm n'apparaît plus, ce qui démontre que dans ces conditions, l'acide polywolframique T (transitoire) ne se forme pas ;

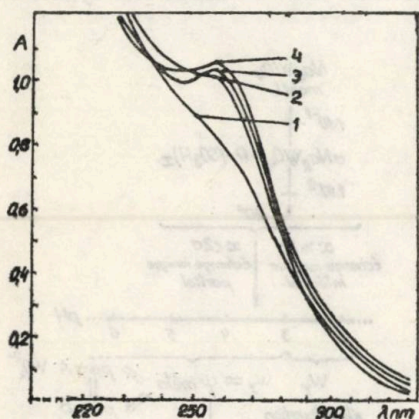


Fig. 5. — Spectres d'absorption en UV enregistrés en fonction du temps sur une solution de sels et d'acides polywolframiques (obtenus par échange ionique partiel) à la température ordinaire : 1 — solution fraîche, 2 — solution à 5 jours, 3 — solution à 25 jours, 4 — solution à 50 jours depuis la préparation ; $C_{\text{WO}_3}^{(3)} = 5 \cdot 10^{-2}$ mols/l, $\text{pH} = 3,6$; cuve = 1 cm.

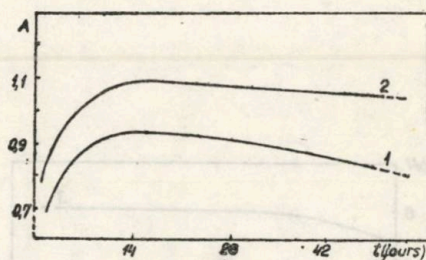


Fig. 6. — Courbes $A = f(t)$ de quelques solutions contenant des sels et des acides polywolframiques (obtenus par échange ionique partiel) pour $\lambda_{\text{max}} = 258$ nm : 1 — $\text{pH} = 3,6$, 2 — $\text{pH} = 5,4$; $C_{\text{WO}_3}^{(3)} = 5 \cdot 10^{-2}$ mols/l.

b) en échange, la bande d'absorption à $\lambda_{\text{max}}=258$ nm se développe normalement, ce qui confirme la formation dans le temps de l'anion de l'acide métawolframique.

À chaud, la stabilisation des solutions de sels et d'acides polywolframiques découle rapidement, approximativement en 1 h, à $95^\circ \dots 98^\circ\text{C}$.

2.4. Détermination du pH

Dans le processus de stabilisation des solutions des combinaisons polywolframiques (obtenues par échange ionique) le pH se modifie relativement peu (Fig. 7). Ainsi, la stabilisation de la solution ayant un $\text{pH}=2,4$ est accompagnée d'une augmentation à peine perceptible de la concentration en ions H^+ , tandis que pour les solutions ayant un $\text{pH}=3,6$ et $5,4$ la concentration en ions H^+ décroît.

2.5. Synthèse de l'acide métawolframique

Les déterminations spectrophotométriques prouvent que pendant la stabilisation des solutions de combinaisons polywolframiques, dans un large domaine de valeurs du pH, c'est l'acide métawolframique, éventuellement son sel qui se forme (Fig. 8).

Il s'ensuit que l'échange ionique dans le système Na_2WO_4 (en solution) — Amberlithe IR 120(H^+) peut constituer une méthode de synthèse de l'acide métawolframique.

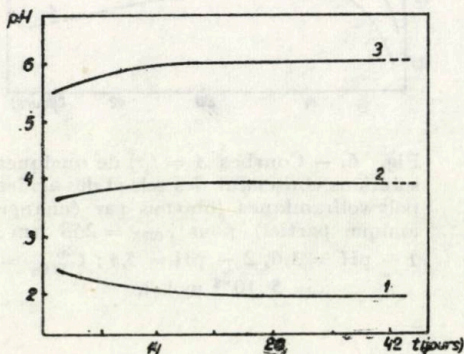


Fig. 7. — Courbes $\text{pH} = f(t)$ de quelques solutions contenant des sels et des acides polywolframiques résultés par échange ionique : 1 — $\text{pH}(\text{initial}) = 2,4$; 2 — $\text{pH} = 3,6$, 3 — $\text{pH} = 5,4$; $C_{\text{WO}_3}^{(3)} = 5 \cdot 10^{-2}$ mols/l.

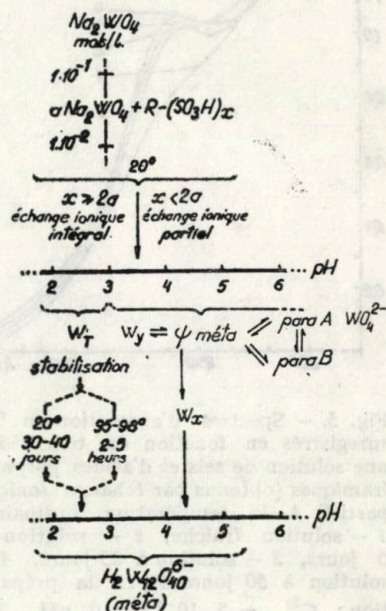


Fig. 8. — Schéma des processus de formation et de stabilisation des combinaisons polywolframiques dans le système Na_2WO_4 (en solution) — Amberlithe IR 120 (H^+).

Les conditions de synthèse de l'acide métawolframique découlent des données expérimentales présentées ci-dessus. Ainsi, dans des solutions de concentration $1 \cdot 10^{-1} \dots 1 \cdot 10^{-2}$ mols/l Na_2WO_4 , ou plus diluées et à un $\text{pH} = 3,5 \dots 4$, à $95^\circ \dots 98^\circ\text{C}$, l'anion de l'acide métawolframique se forme dans une heure. On ne recommande pas des solutions à un pH plus bas, par exemple 2,4, parce que pendant la synthèse il se précipite une quantité d'acide wolframique et la durée de la synthèse est plus longue.

a) Mode de travail

À une solution qui contient 1 ... 2% Na_2WO_4 on ajoute, en petites portions et en agitant, l'Amberlithe IR 120(H^+), jusqu'au $\text{pH} \approx 3,5$. On

élimine la résine et on chauffe la solution à 95° ... 98°C, approximativement une heure. Pendant ce temps, le pH croît jusqu'à 4,5 ... 5,0 et la solution contient surtout du métawolframate de sodium. On continue l'addition d'Amberlithe IR 120(H⁺), jusqu'à ce que le pH de la solution devient constant (échange intégral). On élimine la résine et on continue à chauffer la solution. Après une heure la solution ne contient que de l'acide métawolframique. On effectue la concentration de la solution jusqu'à ce que le liquide devient visqueux et des cristaux d'acide métawolframique apparaissent. Avant d'arriver au sec on passe la pâte sur une plaque poreuse et on presse légèrement avec une spatule en plastique. Les cristaux d'acide métawolframique apparus sont gardés dans une fiole fermée. Le rendement est très bon et l'acide métawolframique n'est pas impurifié par de l'acide wolframique.

3. Conclusions

L'échange ionique dans le système Na₂WO₄ (en solution) — Amberlithe IR 120(H⁺) conduit à une série de sels et d'acides polywolframiques semblables à ceux qu'on obtient en acidulant les wolframates avec les acides minéraux forts (HNO₃, HCl, etc.). Par la stabilisation de ces solutions il se forme, dans un intervalle large de pH, l'anion de l'acide métawolframique. En partant de cet échange ionique on a élaboré une méthode de synthèse pour l'acide métawolframique, d'une pureté avancée et à un très bon rendement.

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SCHIMBUL IONIC ÎN SISTEMUL Na_2WO_4 (SOLUȚIE) — AMBERLIT IR 120 (H^+)

I. Acidul metawolframic

(Rezumat)

Schimbul ionic prin metoda statică în sistemul Na_2WO_4 (soluție) — Amberlit IR 120 (H^+) conduce la o serie de săruri și acizi poliwolframici asemănători celor obținuți la acidularea wolframaților cu acizi minerali tari (HNO_3 , HCl etc.). În schimb, folosirea rășinii produce soluții cu compuși poliwolframici puri și limitează numărul protonilor la cei indicați de stoechiometria globală a reacției, oricare ar fi excesul de rășină.

În acest schimb ionic, la concentrații $1 \cdot 10^{-1} \dots 1 \cdot 10^{-2}$ moli/l Na_2WO_4 (cît și în afara acestor limite) și la un $\text{pH} \approx 2 \dots 3$, apare tranzitoriu, în soluții proaspete, o specie care a fost numită acid poliwolframic T.

Prin stabilizarea acestor soluții timp de 30...40 zile (sau mai repede la cald) se formează, într-un domeniu larg de pH ($\approx 2,4 \dots 5,4$), anionul acidului metawolframic. Această observație stă la baza unei metode de sinteză a acidului metawolframic.

THEORETICAL AND EXPERIMENTAL ASPECTS CONCERNING INDIRECT DETERMINATION OF Ni^{2+} USING THE CYAN-SENSITIVE ELECTRODE (I)

BY

FLORICICA MATEI, GH. IONESCU, EUGENIA DONIGA and AL. DUCA

1. Introduction

Remarkable theoretical and practical progresses were made in using ion-sensitive electrodes in quantitative analytical dosing. Numerous papers and patents are reported concerning with theoretical principles the ion-sensors are based on, their performance and applications.

The ion-sensitive electrodes are suitable for the indirect analytical determinations. The indirect determinations were applied and their advantages mentioned in previous papers [1]...[5].

The Ni^{3+} ion gives rather stable complexes with CN^- anion. Based on this fact the CN-sensitive electrode is used for indirect determination of Ni^{2+} ions in concentration of the $\mu\text{g/l}$ order. This shifting of the concentration to the micrograms range is determined by one of the optimum conditions of the electrode operation, namely $\text{pH} > 10$ [6]...[12]. At such a high pH value the Ni^{2+} ions precipitate as $\text{Ni}(\text{OH})_2$. Consequently, the maximum concentration of the solubility product of $\text{Ni}(\text{OH})_2$ in that medium is obtained.

The aim of these paper is to draw and linearize a calibration curve for CN^- determination with a CN-sensitive electrode, to linearize some standard curves for the Ni^{2+} indirect analysis starting from different initial CN^- concentrations as well as to test the method reproductibility within the low concentration range.

2. Experimental

The experiments were run in a cell thermostated at 25°C , under magnetical stirring at 100 rot./min. and the EMF read after stopping the stirring. The solution ionic strength was kept constant at 0.7 mol/l (with a 2M KNO_3 solution) and $\text{pH} = 13$ (with a 0.25 M NaOH solution). During experiments the ionic strength modified with no more than 2%.

2.1. Reagents and Equipment. Measuring Method

The stock solutions were prepared with reagents of p.a. grade and bidistilled water. The KCN solution was standardized potentiometrically with AgNO_3 by using a CN-sensitive electrode as indicator electrode and the $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ solution, gravimetrically, with DMG.

The CN-sensitive electrode of the Radelkis OP-CN-7112D (Hungary) type and the reference one (s.c.e.) were supplied by the same firm.

The EMF was measured by means of a pH-meter MV-84, Prăcitronic (GDR), with ± 700 mV, ± 350 mV and ± 70 mV measuring ranges.

The measuring method is based on the using of a CN^- solution having a given concentration to which portions of solution containing Ni^{2+} were added. Due to binding of CN^- in complexes $[\text{Ni}(\text{CN})]^{(n-2)-}$, the EMF decreases remaining constant after the appearance of a stable $\text{Ni}(\text{OH})_m$ precipitate.

The EMF may be correlated with both $c(\text{CN}^-)$ and $c(\text{Ni}^{2+})$ concentrations. These functions may be adjusted in convenient coordinates and used as calibration curves.

2.2. Calibration Curve $E - c(\text{CN}^-)$

It is necessary to know the concentration of CN^- ions for calculating both the concentration of Ni^{2+} ions and the stability constants of $\text{Ni}(\text{CN})_m$ complexes. For this reason KCN solutions of concentrations within the $1 \cdot 10^{-2} \dots 4 \cdot 10^{-6}$ mol/l range were prepared and their EMF (E) measured the results being given in Table 1.

Table 1
EMF as a Function of $c(\text{CN}^-)$ *

$c(\text{CN}^-)$, [mol/l]	4×10^{-6}	1×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}	1×10^{-3}	5×10^{-3}	1×10^{-2}
pCN	5.40	5.00	4.30	4.00	3.30	3.00	2.30	2.00
E , [mV]	-35	-63	-110	-130	-172	-188	-233	-250

*) E is the average of three measurements.

Based on these data the linear function $E - p\text{CN}$ was obtained (Fig. 1) with a slope differing by about 6% from the theoretical value since the concentration was used instead of the activity.

By using the statistical method of data processing [13] the equation of this calibration curve is obtained namely

$$E = 62.8 p\text{CN} - 377.7, [\text{mV}],$$

$$(s_0^2 = 6.587; n = 8; P = 95\% ;$$

$$\Delta a = 7.4 \text{ and } \Delta b = 1.9).$$

2.3. Calibration Curve $E - c(\text{Ni}^{2+})$ for Ni^{2+} Indirect Analysis

Since two ligands (OH^- and CN^-) compete to the Ni^{2+} complexation in cyanide alkaline solutions the solubility product of the hydroxycomplex

[9] is expected to increase in the presence of CN^- since the $\text{Ni}(\text{CN})_n$ complexes are more stable (e.g. $pK = 4 \times 10^4$ for NiOH^+ and $pK = 1 \times 10^{22}$ for Ni

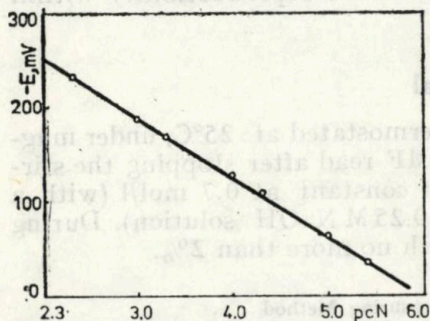


Fig. 1. - Calibration curve $E - p\text{CN}$.

(CN⁻)₄ [14], [15]. This fact affords for enlarging the indirect analysis range for the low Ni²⁺ concentrations in strong alkaline solutions using the CN-sensitive electrode.

In the presence of Ni²⁺ the concentration of the free CN⁻ ions towards which the electrode is sensitive is given by the equilibrium $n\text{CN}^- + \text{Ni}^{2+} \rightleftharpoons [\text{Ni}(\text{CN}^-)_n]^{(n-2)-}$. This equilibrium shifts to the right as the Ni²⁺ total concentration increases. Consequently, the EMF is a function of the Ni²⁺ total concentration. Such a correlation permits to draw the calibration curve in the $E - f(\text{Ni}^{2+} \text{ total concentration})$ coordinates for the Ni²⁺ indirect analysis with the CN-sensitive electrode. This function will be rather complicated since the relation between the concentration of the free CN⁻ ions and the total concentration of the Ni²⁺ ions is complicated as it is evident in the following set of equations:

$$c_n = K_n c_1^n c_2, \quad c_2 = c_{02} - c_n, \quad c_1 = c_{01} - n c_n,$$

where: n is the number of the CN⁻ groups in the complex; c_n , c_1 and c_2 — equilibrium concentration of the $[\text{Ni}(\text{CN}^-)_n]^{(n-2)-}$, CN⁻ and Ni²⁺, respectively; K_n — stability constant of the complex; c_{01} and c_{02} — initial concentrations of the CN⁻ and Ni²⁺ ions, respectively.

By solving these equations one obtains:

$$c_1 = c_{01} - \frac{n K_n c_{02}}{1/c_1^n - K_n}.$$

The EMF of the CN⁻ selective electrode depends on the concentration c_1 according to the relationship:

$$E = E_0 - \frac{RT}{F} \ln c_1$$

and consequently the following equation may be considered for the $E - c_{02}$ function:

$$(1) \quad E = E_0 - \frac{RT}{F} \ln \left(c_{01} - \frac{n K_n}{1/c_1^n + K_n} c_{02} \right).$$

This equation may be simplified depending on the c_{01} , c_{02} , c_n and K_n values. For $(c_{01}/c_{02})_{\max} > 4$ the $[\text{Ni}(\text{CN}^-)_4]^{2-}$ complex formation is assured and $n = 4$. For $K_1 \gg 1/c_1^4$ the equation (1) becomes linear in the $E - \ln(c_{01} - 4c_{02})$ coordinates and takes the form:

$$(2) \quad E = E_0 - \frac{RT}{F} \ln (c_{01} - 4c_{02}).$$

The experimental data given in Table 2 and depicted after processing in Fig. 2, fit the equation (2). By statistical processing the following values for the straight line parameters were obtained: $E_0 = -383$ mV, $RT/F = 28.6$ J/C (dispersion $s_0^2 = 0.253$; $n = 10$; $P = 95\%$; $\Delta E_0 = 3$ mV and $\Delta(RT/F) = 0.6$). Consequently, the straight line equation may be written:

$$(3) \quad E = -383 - 28.6 \ln (c_{01} - 4c_{02}), [\text{mV}].$$

Table 2

Experimental E and c_{02} Data for $c_{01} = 1.86 \cdot 10^{-2}$ mol/l

$10^4 c_{02}, [\text{mol/l}]$	6.65	9.96	13.27	16.56	20.66	24.75	28.83	32.90	36.95	40.98
$-E, [\text{mV}]$	265	262	259	256	252	248	242	234	223	208

Theoretically, $RT/F = 25.7$ J/C at 25°C . The difference of about 10% between the experimental and theoretical values is due to using the CN^- concentration instead of activity.

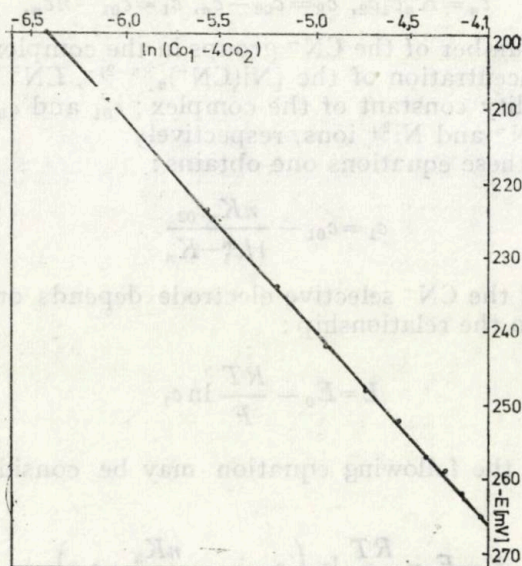


Fig. 2. — Verification of the theoretical equation (7).

By using values between 10^{-4} and 10^{-3} mol/l for c_{01} , the maximum concentration for Ni^{2+} in concentrated solutions is found experimentally to be high enough for the $(c_{01}/c_{02})_{\text{max}}$ ratio not to exceed 2 ... 2.5. Under these conditions the probability of formation is higher for the complex $\text{Ni}(\text{CN}^-)_2$ and the equation of type (2) is not linear (Fig. 3). It results that $1/c_1^2$ has a value comparable to that of the stability constant K_2 ; as a consequence is not possible to simplify the equation (1).

Such a concentration range for CN^- may be however useful for extending the Ni^{2+} analysis range to the lower concentration values. For this range the calibration curves may be used without knowing the stability constants of the $[\text{Ni}(\text{CN}^-)_n]^{(n-2)-}$ complexes which might form; the coordinates of these diagrams were settled by processing the experimental data.

For initial concentration, $c_{01} = 1.1 \times 10^{-3}$ and 5.3×10^{-4} mol/l the linear diagrams have the same coordinates, namely $E - c^2(\text{Ni}^{2+})$. In Figs. 4 and 5 the linear diagrams for these concentrations are represented.

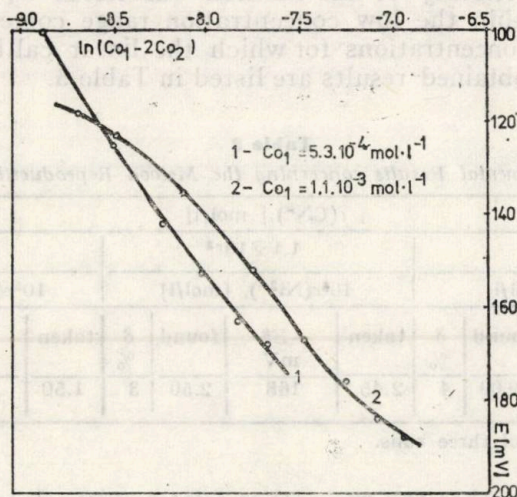


Fig. 3. — Non-linear coordinates for the equation (2).

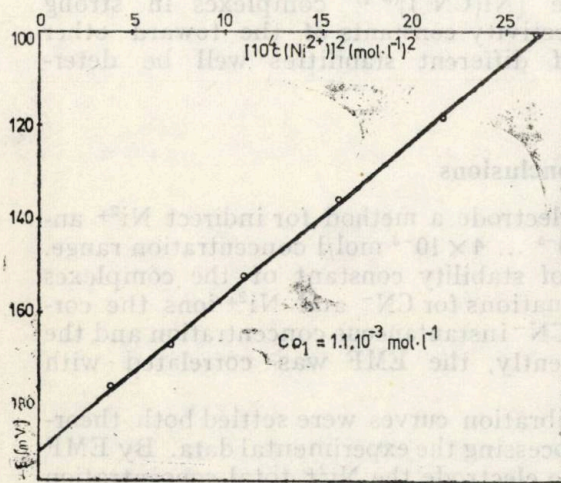


Fig. 4. Linear calibration curve for $c_{01} = 1.1 \times 10^{-3}$ mol/l.

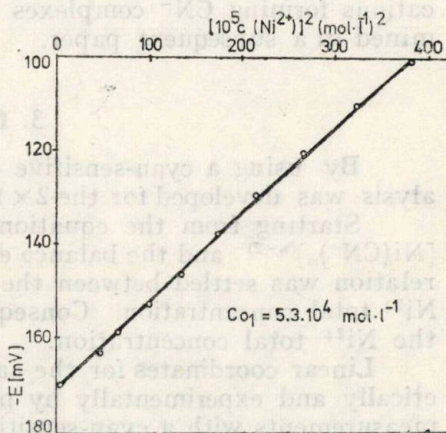


Fig. 5. — Linear calibration curve for $c_{02} = 5.3 \times 10^{-4}$ mol/l.

The equations for these straight lines, derived by statistical processing of the experimental data, are the following :

$$E = -189 + 3.30[10^5 c(\text{Ni}^{2+})]^2, [\text{mV}], (\text{s. Fig. 4}),$$

$$(s_0^2 = 0.790 ; n = 8 ; P = 95\% ; \Delta a = 0.1 \text{ and } \Delta b = 0.07) ;$$

$$E = -170.9 + 0.184[10^5 c(\text{Ni}^{2+})]^2, [\text{mV}], (\text{s. Fig. 5}),$$

$$(s_0^2 = 1.013; n = 8; P = 95\%; \Delta a = 0.98 \text{ and } \Delta b = 0.005).$$

The reproductibility of the method was tested by analysing three Ni^{2+} solutions within the low concentration range corresponding to the three CN^- initial concentrations for which the linear calibration diagrams were drawn. The obtained results are listed in Table 3.

Table 3
Experimental Results concerning the Method Reproducibility

$c(\text{CN}^-), [\text{mol/l}]$											
5×10^{-4}				1.1×10^{-3}				1.86×10^{-2}			
$10^5 c(\text{Ni}^{2+}), [\text{mol/l}]$				$10^4 c(\text{Ni}^{2+}), [\text{mol/l}]$				$10^2 c(\text{Ni}^{2+}), [\text{mol/l}]$			
taken	$-E^*$ mV	found	δ %	taken	$-E^*$ mV	found	δ %	taken	$-E^*$ mV	found	δ %
8.66	156	9.00	4	2.45	168	2.50	3	1.50	257	1.54	3

*) the average of three runs.

It can be seen that the percentage relative error does not exceed 4%, even in the range of low Ni^{2+} concentrations ($8.66 \times 10^{-5} \text{ mol/l} = 5 \mu\text{g/l} = 5 \text{ ng/cm}^3$).

The stability constants of the $[\text{Ni}(\text{CN}^-)]^{(n-2)-}$ complexes in strong alkaline media as well as the selectivity constants of the toward other cations forming CN^- complexes of different stabilities well be determined in a subsequent paper.

3. Conclusions

By using a cyan-sensitive electrode a method for indirect Ni^{2+} analysis was developed for the $2 \times 10^{-5} \dots 4 \times 10^{-3} \text{ mol/l}$ concentration range.

Starting from the equation of stability constant of the complexes $[\text{Ni}(\text{CN}^-)_n]^{(n-2)-}$ and the balance equations for CN^- and Ni^{2+} ions the correlation was settled between the CN^- instantaneous concentration and the Ni^{2+} total concentration. Consequently, the EMF was correlated with the Ni^{2+} total concentration.

Linear coordinates for the calibration curves were settled both theoretically and experimentally by processing the experimental data. By EMF measurements with a cyan-sensitive electrode the Ni^{2+} total concentration may be then measured in a solution also containing CN^- ions.

The method is fast and shows a good reproductibility, the percentage relative error being of about 4% for low Ni^{2+} concentrations.

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ASPECTE TEORETICE ȘI EXPERIMENTALE PRIVIND DETERMINAREA
INDIRECTĂ A IONILOR Ni^{2+}

(Rezumat)

Ca urmare a stabilității mari a complexilor $\text{Ni}(\text{CN}^-)^{(n-2)-}$ se propune o metodă indirectă de analiză a ionilor Ni^{2+} , utilizând un electrod cian-sensibil, a cărui t.e.m. variază ca urmare a formării complexelor de forma specificată. Se stabilește o ecuație între t.e.m. a electrodului și concentrația totală a Ni^{2+} din soluția analizată, ecuație care devine liniară pentru $c(\text{CN}^-)/c(\text{Ni}^{2+}) \geq 4$. Pentru $c(\text{CN}^-)/c(\text{Ni}^{2+}) < 4$ au fost stabilite ecuații liniare empirice, utile pentru extinderea domeniului de concentrație în care Ni^{2+} poate fi analizat cu ajutorul acestei metode. Metoda propusă este rapidă, sensibilă și suficient de reproductibilă. Astfel, chiar la concentrații mici (de ordinul $8 \cdot 10^{-5}$ mol/l), eroarea relativă nu depășește 4%.

**$^{60}\text{Co(II)}$ AND Ni(II) SORPTION ON
 $p(\text{BENZYLCELLULOSE})\text{-5-AZO-8-HYDROXYQUINOLINE}$**

BY

TINCA UNGURENAȘU, SIMON FIȘEL and AL. CECAL

1. Introduction

The functional group 8-hydroxyquinoline present in a polymer matrix gives to the resins a selectivity for some elements. There were synthesised such chelating resins that used to separate different elements [1] ... [4].

In what follows there are presented the synthesis of a chelating polymer based on cellulose that contains azo and 8-hydroxyquinoline groups, the mechanism of sorption of $^{60}\text{Co(II)}$ and Ni(II) and the possibility of concentration of the two metals on this sorbent.

2. Experimental

$p(\text{Benzylcellulose})\text{-5-azo-8-hydroxyquinoline}$ was synthesised from PAB-cellulose diazotized and coupled with 8-hydroxyquinoline. For diazotization, 2 g of PAB-cellulose were mixed with 50 ml of cold 2 N HCl (0°C) and 10 ml of 14% NaNO_2 and left at 0°C for an hour. The diazonium salt obtained was filtered and washed with a solution of 5% CH_3COONa , 5% urea and finally with water. For coupling there were used 2 g 8-hydroxyquinoline(oxine) that were treated with some solution of 2 N NaOH and water obtaining 2 l solution with $\text{pH} \approx 8$. Diazotized cellulose was mixed with the solution of 8-hydroxyquinoline by mechanical stirring at 0°C for 10 hours. The sorbent was washed with water till neutral reaction.

For the establishing of sorption mechanism of $^{60}\text{Co(II)}$ and Ni(II) on this sorbent were made the following determinations:

1. Dependence of pH, distribution coefficients at 25°C .
2. Sorption isotherms at 25°C .
3. Sorption isobars between 0° and 100°C .
4. Determination of apparent free enthalpy of the exchange reaction.
5. IR spectra of the sorbent before and after sorption between 400 and 4000 cm^{-1} .

The distribution coefficients have been determined statically by stirring at 25°C for one hour 0.2 g sorbent as R—Na form with 10 ml standard solution of cobalt nitrate ($59.94 \mu\text{g } ^{60}\text{Co(II)}/\text{ml}$) and nickel nitrate ($58.48 \mu\text{g Ni(II)}/\text{ml}$) with a certain pH. After installation of the equilibrium (one hour) the phases were separated by filtration. The equilibrium pH (pH_e) was measured in the aqueous phase. In an aliquot of the filtrate the excess of Ni(II) was determined by atomic absorption spectrophotometry and the excess of $^{60}\text{Co(II)}$ was measured with a Geiger-Müller γ -counter (MC-6) connected to an electronic scaler VSP-1960.

3. Results and Discussions

From the investigation of the distribution coefficients (K_d) function of pH, results that $^{60}\text{Co(II)}$ sorption increases gradually from $\text{pH}_e = 1.25$ to $\text{pH}_e = 5.75$ ($K_d = 5.13 \cdot 10^2$) and Ni(II) sorption from $\text{pH}_e = 1.5$ to $\text{pH}_e = 6.65$ ($K_d = 2.4 \cdot 10^2$).

The sorption isotherms of $^{60}\text{Co(II)}$ and Ni(II) (Fig. 1) have forms that plead for a combined process of adsorption and chemisorption, the last being prevalent especially in the case of $^{60}\text{Co(II)}$.

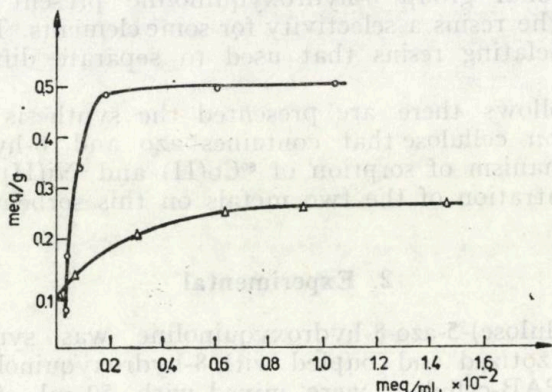


Fig. 1. — The sorption isotherms at $\text{pH}_e = 5.5...5.75$ and 25°C: $\circ$ — $^{60}\text{Co(II)}$; Δ — Ni(II).

The same conclusion follows from sorption isobars (Fig. 2). A decrease of the distribution coefficients due to the partial solubility of metallic oxinats may be noticed between 25°...100°C. At 100°C this phenomenon is accompanied by the partial degradation of the sorbent.

The apparent free enthalpy was calculated from relation

$$\Delta G = -RT \ln K,$$

where K is a constant of the exchange reaction that was calculated by Nikolski's method [5].

The values of the apparent free enthalpy (-2825 cal/mol of $^{60}\text{Co(II)}$ and -1141 cal/mol of Ni(II)) show the existence of an ionic exchange that is more prominent in the case of Co(II).

The IR spectra are difficult to be interpreted because the small differences in the form and displacement of the peaks. In spectrum of *p*(benzylcellulose)-5-azo-8-hydroxyquinoline appears a peak at 1580 cm^{-1} attrib-

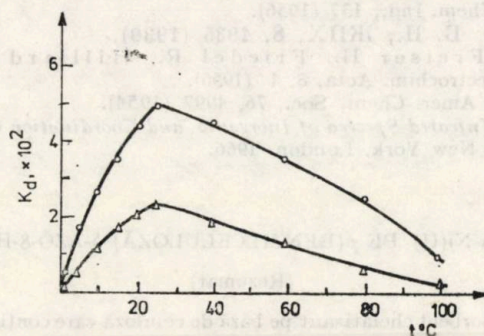
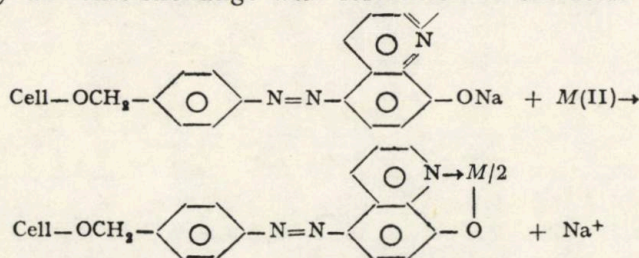


Fig. 2. — The sorption isobars between 0...100°C: ○ — $^{60}\text{Co(II)}$; Δ — Ni(II) .

uted to the azo group. This does not modify the compound treated with Co(II) or Ni(II) , so the azo group does not participate to the formation of chelates. The modification or disappearance of the vibration characteristic to the OH group from 8-hydroxyquinoline cannot be set off because of the presence of the unmodified OH groups from cellulose. But the vibration characteristic to the chain C—O (1200 cm^{-1}) and C—N ($1300\text{...}1400\text{ cm}^{-1}$) shift smaller wavenumbers due to the new interactions between electronic orbitals of Co(II) and Ni(II) and those of oxygen and nitrogen atoms in the formed compounds [6]...[8].

The obtained data by equilibrium method and IR spectra led to the conclusion that the physic sorption of Co(II) and Ni(II) is accompanied by a chemical one, the last being prevalent. Probably, the chemical sorption take place by an ionic exchange with formation of chelates:



p(Benzylcellulose)-5-azo-8-hydroxyquinoline permits the concentration of Co(II) and Ni(II) using small quantities of sorbent. So, on 0.2 g sorbent at $\text{pH}=5.5\text{...}5.7$ can be concentrated 2.8 mg Co(II) and 1.6 mg Ni(II) at $\text{pH}=6$ from diluted solutions. The desorption of the two elements is made with 0.1 M HNO_3 .

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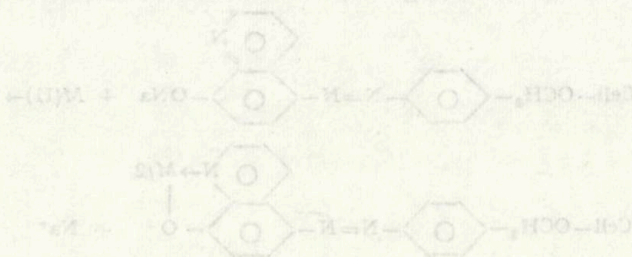
SORBȚIA $^{60}\text{Co(II)}$ ȘI A Ni(II) PE $p(\text{BENZILCELULOZĂ})\text{-5-AZO-8-HIDROXICHINOLINĂ}$

(Rezumat)

S-a sintetizat un sorbent chelatizant pe bază de celuloză care conține grupa azo și 8-hidro-xichinolină.

S-a cercetat mecanismul sorbției $^{60}\text{Co(II)}$ și a Ni(II) pe $p(\text{benzilceluloză})\text{-5-azo-8-hidroxi-chinolină}$. Din studii variației coeficienților de distribuție față de pH, izotermelor și izobarelor de sorbție, spectrelor IR și valorilor entalpiei libere aparente, rezultă că sorbția fizică a $^{60}\text{Co(II)}$ și a Ni(II) este însoțită de o reacție cu formare de chelați.

Utilizând cantități mici de sorbent, cele două elemente pot fi concentrate din soluții diluate.



$p(\text{Benzilceluloză})\text{-5-azo-8-hidroxi-chinolină}$ permite concentrarea $^{60}\text{Co(II)}$ și Ni(II) din soluții diluate. Se obțin izoterme de sorbție la pH = 5.5-5.7 care pot fi utilizate pentru concentrarea $^{60}\text{Co(II)}$ și Ni(II) din soluții diluate. Se obțin izoterme de sorbție la pH = 5.5-5.7 care pot fi utilizate pentru concentrarea $^{60}\text{Co(II)}$ și Ni(II) din soluții diluate. Se obțin izoterme de sorbție la pH = 5.5-5.7 care pot fi utilizate pentru concentrarea $^{60}\text{Co(II)}$ și Ni(II) din soluții diluate.

CONTRIBUTIONS TO THERMAL DEGRADATION OF SOME COMPLEX COMBINATIONS OF Pd(II) WITH PROLINE

BY

NATALIA HURDUC and OLGA VICOL

1. Introduction

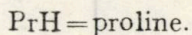
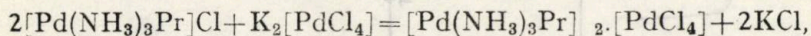
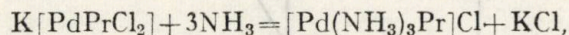
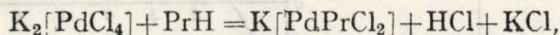
Very few data about the synthesis and characterization of the complex combinations of Pt(II) and Pd(II) with proline are known in the literature. It is possible to be mentioned the works of Volstein and coworkers [1] presenting the methods to obtain some combinations of Pt(II) with proline and some properties they exhibit as well as our works [2], [3] referring to the synthesis of some combinations of Pd(II) with the same aminoacid and their characterization.

From these works it results that the bond of the proline to the central metallic ion is done through the imino group and the deprotonized carboxylic group when the ligand acts as a bidentate, or through the iminic nitrogen if the ligand is monodentate one.

To complete the study concerning the complex combinations of Pd(II) with proline, the aim of these paper is to study the thermogravimetric behaviour of the $K[PdPrCl_2]$ and $[Pd(NH_3)_3Pr]_2[PdCl_4]$ compounds and to suggest the mechanism of thermal degradation pertaining to these combinations.

2. Theoretical

From previous studies it results that these combinations results from the reactions :



3. Experimental

The synthesized combinations were characterized by elementary analysis and the results are concentrated in Table 1.

The thermogravimetric study was carried out on a derivatograph MOM—Budapest in dynamic conditions, using a heating rate of 12.4°C/min.

Table 1
Elementary analysis of Pd(II) Complexes with Proline

Compound	Pd		N	
	calculated %	found %	calculated %	found %
$K[PdPrCl_2]$	32.12	31.80	4.23	4.75
$Pd(NH_3)_3Pr]_2 \cdot [PdCl_4]$	40.24	40.90	14.12	14.02

The kinetic processing of the thermogravimetric data is based on the Freeman-Carroll's method [4], [5]. The thermogram for proline, as presented in Fig. 1, shows the complete degradation until 600°C in a single step.

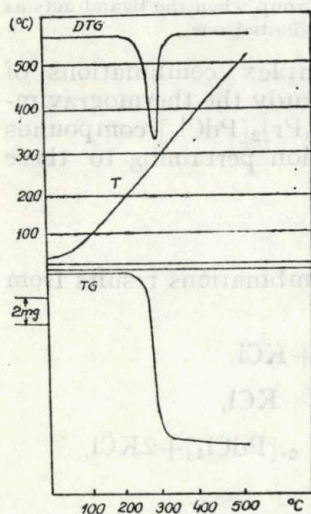


Fig. 1. — Thermogram of proline; degradation in air; heating rate 124°C/min.

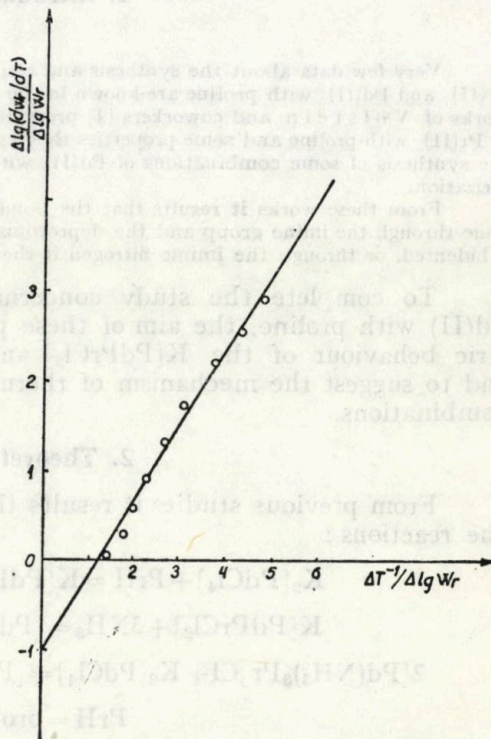


Fig. 2. — Freeman-Carroll diagram for proline.

The diagram represented in Fig. 2 was obtained by applying the Freeman-Carroll's methods and shows an order of reaction equal to unity and an activation energy of 153.8 KJ/mol.

For complex combinations the degradation occurs in more steps, as shown in Fig. 3.

By applying the differential Freeman-Carroll's method the diagrams shown in Figs. 4 and 5 were obtained.

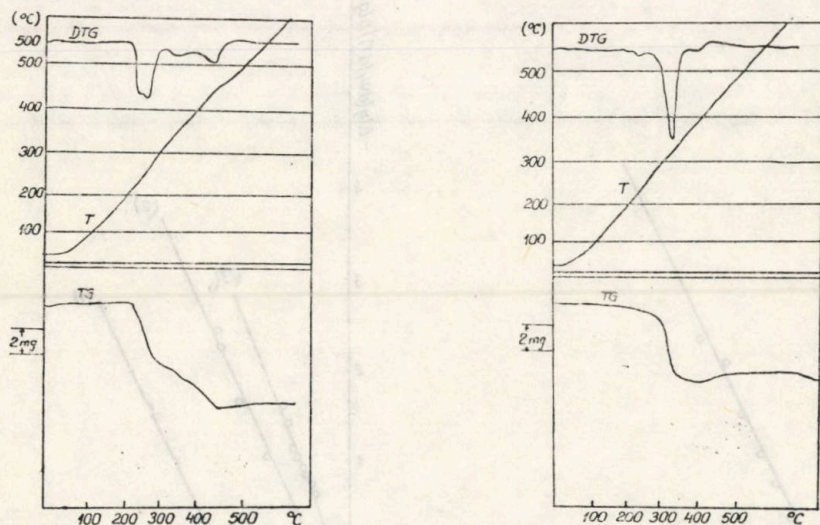


Fig. 3. — Thermograms of the Pd (II) complexes with proline ; degradation in air ; heating rate 12.4°C/min.

Table 2

Kinetic Characteristics of Thermal Degradation of Pd(II) Proline Compounds

Compound	Degradation range temperature °C	Kinetic parameters	
		E, [KJ/mol]	n
Proline	120...136	153.8	1
K[PdPrCl ₂]	200...315	192.2	3
	315...390	232.2	1
	390...402	275	0.5
[Pd(NH ₃) ₃ Pr] ₂ · [PdCl ₄]	120...250	192.2	0.5
	250...390		

Calculating the kinetic parameters we obtain the values shown in Table 2. One can ascertain the complex character of the thermic degradation for these combinations based on the increase of the activation energy with the temperature range within which the degradation takes place.

The elementary analysis of the intermediates and residuals was performed and the results are tabulated in Table 3. Correlating these results

with the kinetic and thermogravimetric characteristics we suggest that the mechanism of the thermic degradation of the studied compounds may be of the form represented in Fig. 6.

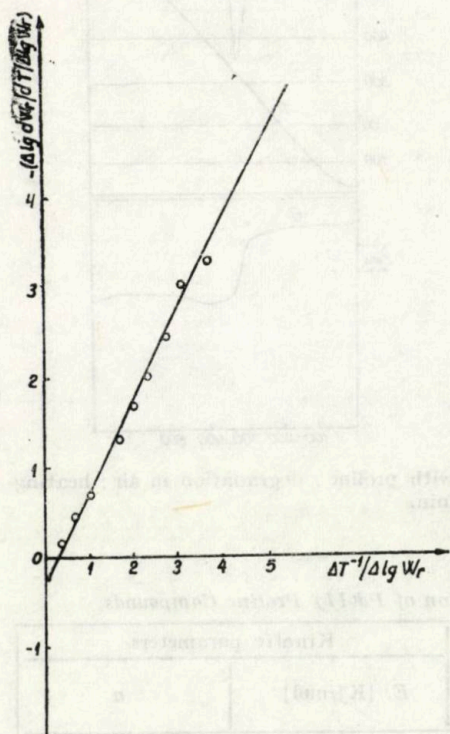


Fig. 4. — Freeman-Carroll diagram for $[\text{Pd}(\text{NH}_3)_3\text{Pr}]_2 \cdot [\text{PdCl}_4]$.

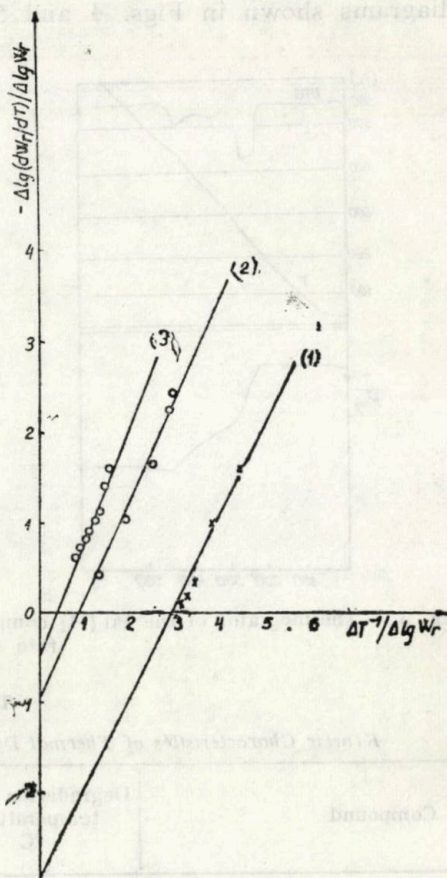


Fig. 5. — Freeman-Carroll diagram for $\text{K}[\text{PdPrCl}_2]$.

Table 3
Elementary Analysis of the Intermediate and Final Compounds

Starting compound	Intermediate compound separation temperature °C	Pd		Residual	Pd	
		calc. %	found %		calc. %	found %
$\text{K}[\text{PdPrCl}_2]$	315	38.15	38.90	$\text{PdO} + \text{KCl}$	54.16	56.23
$[\text{Pd}(\text{NH}_3)_3\text{Pr}]_2[\text{PdCl}_4]$	250	42.82	43.20	$2\text{PdO} + \text{PdCl}_2$	75.67	76.30

In all intermediates chlorine was found but a quantitative analysis was not possible because of the smallness of the samples.

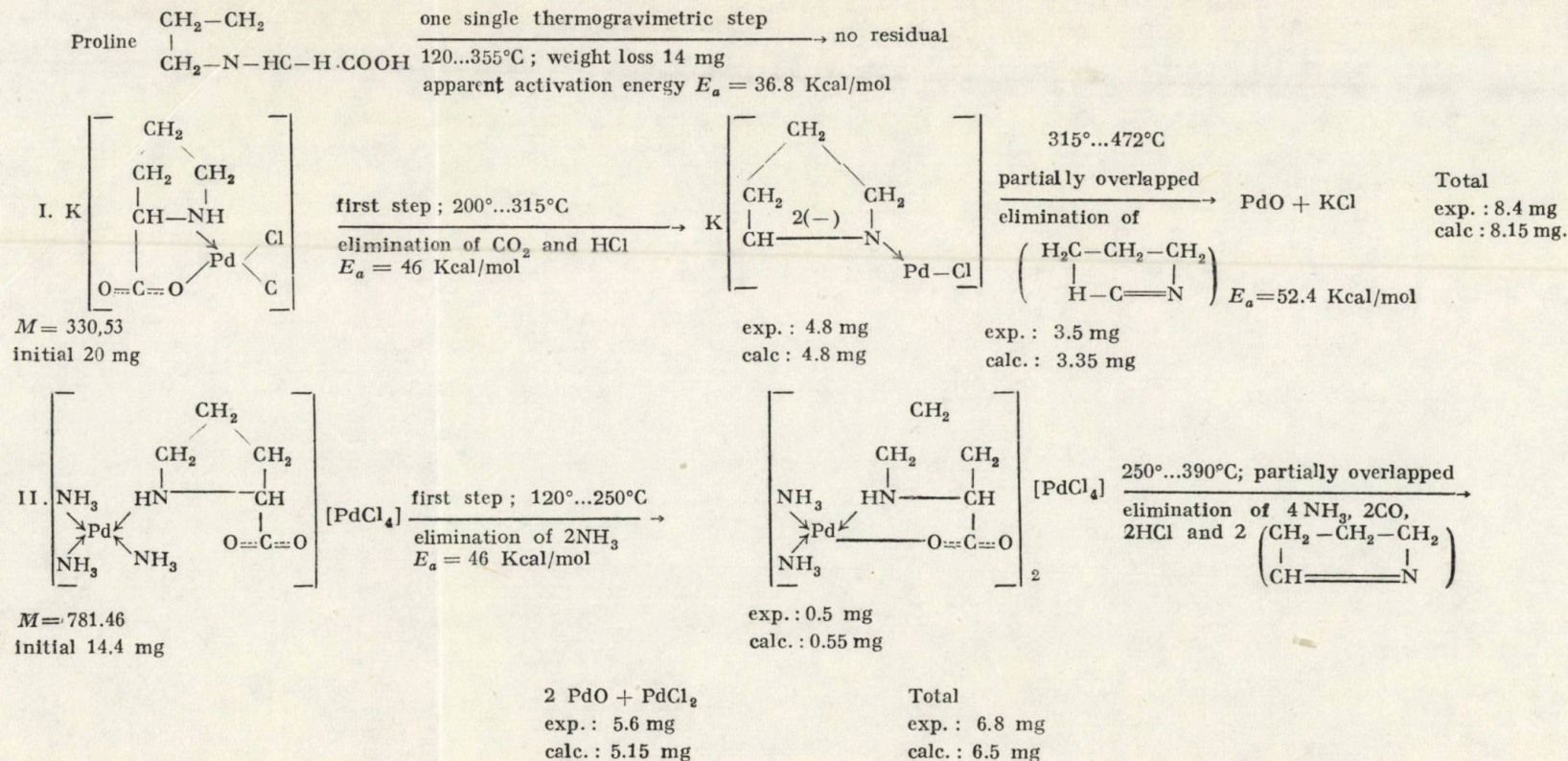


Fig. 6. — Schema of the thermal degradation in air of Pd(II) — proline complexes at a heating rate of 12.4°C/min.

4. Conclusions

It was studied the thermogravimetric behaviour of two new complex combinations of Pd(II) with proline.

Correlating the results of the kinetic and thermogravimetric characteristics a mechanism of the thermic degradation of the studied compounds is proposed.

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CONTRIBUȚII LA DEGRADAREA TERMICĂ A CÎTORVA COMBINAȚII COMPLEXE ALE Pd(II) CU PROLINA

(Rezumat)

Se prezintă rezultatele studiului referitor la comportarea termică a unor combinații complexe ale Pd (II) cu prolina. Pe baza rezultatelor obținute s-au evaluat parametrii cinetici ai reacțiilor studiate și s-a propus o schemă a degradării termice suferite de compușii Pd (II) cu prolina la viteza de încălzire de 12,4°/min.

4. Conclusions

It was studied the thermodynamic behavior of two new complex compounds of Pb(II) with pyrene.
Correlating the results of the kinetic and thermodynamic observations a mechanism of the thermic degradation of the studied compounds is proposed.

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CONTRIBUȚII LA DEGRADAREA TERMICĂ A CITOXA COMBINAȚII COMPLEXE
ALE Pb(II) CU PIREN

(Rezumat)

Se prezintă rezultatele studiului termodinamic la compunerea termică a unor combinații complexe ale Pb(II) cu piren. Pe baza rezultatelor obținute s-a elaborat un mecanism propus al degradării termice a acestor compuși. Se prezintă și rezultatele studiului cinetic al degradării termice a acestor compuși Pb(II) cu piren la viteză de încălzire de 15°C/min.

ÉTUDES OSMOMÉTRIQUES SUR LA COMPATIBILITÉ DES POLYMÈRES EN SOLUTION

PAR

N. AELENEI

1. Introduction

L'interaction thermodynamique entre deux polymères est habituellement appréciée par la valeur du paramètre d'interaction polymère-polymère, χ_{23} . Celui-ci, ayant le même caractère que l'énergie libre de Gibbs, contient des contributions énergétiques — liées aux forces intermoléculaires — et entropiques — liées à la longueur et à la flexibilité des chaînes polymériques. Dans le cas où les forces de dispersion prédominent et les polymères ont des grandes masses molaires, les deux contributions sont positives, défavorables au mélange, de sorte que les couples de polymères soient incompatibles du point de vue thermodynamique, sauf dans le cas où les liaisons hydrogène se forment où lorsque ont lieu des interactions spécifiques par transfert de charge. Cependant, en pratique, on utilise couramment des alliages polymériques relativement homogènes et stables en temps, se trouvant dans un état de pseudo-compatibilité, maintenu par la grande viscosité du système, par l'interpénétration mécanique des chaînes polymériques et, rarement, par l'existence des forces intermoléculaires faibles.

L'introduction d'un troisième composant, à masse molaire réduite (solvant ou plastifiant), produit une diminution du nombre des contacts polymère-polymère et une augmentation de la flexibilité des chaînes, conduisant, pour une concentration donnée, à des systèmes stables du point de vue thermodynamique [1]...[3]. On a montré [3]...[7] que la séparation en phase qui apparaît dans certaines conditions de concentration et température dans un système ternaire solvant (1)-polymère (2)-polymère (3), est produite non seulement par des valeurs positives, suffisamment grandes, du paramètre d'interaction χ_{23} , mais aussi par une différence appréciable entre les paramètres d'interaction χ_{12} et χ_{13} , la grandeur $\Delta\chi = |\chi_{12} - \chi_{13}|$ étant considérée comme une mesure de l'incompatibilité des polymères en solution. La stabilité maximum du système se rencontre dans un solvant ayant la même affinité par rapport aux deux polymères [8].

Il est reconnu unanimement que, pour un couple de polymères donné, la valeur du paramètre d'interaction χ_{23} dépend d'une série de facteurs qui affectent inégalement les deux contributions. Ainsi, la température modifie dans une petite mesure les forces intermoléculaires, mais elle exerce une forte influence sur la flexibilité des chaînes. La nature du solvant, à côté du fait qu'elle peut actionner différemment sur la flexibilité des chaînes des deux polymères, elle peut modifier aussi l'intensité ou la nature des forces intermoléculaires. Les masses molaires et la différence entre la longueur des chaînes affectent la flexibilité et le nombre de contacts entre les deux polymères. Enfin, la concentration affecte le nombre de contacts entre les deux polymères, de sorte que le rapport entre les deux polymères en solution ait un effet décisif sur les valeurs de χ_{23} .

Dans ce qui suit on étudie la dépendance du paramètre d'interaction polymère-polymère, χ_{23} , en fonction de la masse molaire et la proportion

entre les polymères dans un solvant commun. Le paramètre χ_{23} est lié au paramètre d'interaction ternaire, χ_T , défini dans la théorie de Flory-Huggins étendue aux systèmes ternaires, par la relation :

$$(1) \quad \chi_T = \chi_{12} \frac{\bar{\rho}}{\rho_2} w_2 + \chi_{13} \frac{\bar{\rho}}{\rho_3} w_3 - \chi_{23} \frac{\bar{\rho}^2}{\rho_2 \rho_3} w_2 w_3,$$

où : χ_{12} et χ_{13} représentent les paramètres d'interaction polymère-solvant, ρ_2 et ρ_3 — les densités des deux polymères, w_2 et w_3 — les fractions gravimétriques des polymères, $\bar{\rho}$ — la densité moyenne du mélange de polymères ($\bar{\rho} = \rho_2 \rho_3 / (\rho_2 w_3 + \rho_3 w_2)$).

Le paramètre d'interaction ternaire et les paramètres d'interaction polymère-solvant ont été évalués à partir du deuxième coefficient du viriel déterminé à son tour par des mesures osmométriques des systèmes respectivement ternaires et binaires. Le paramètre χ_{23} ainsi déduit est normé au volume d'une molécule de solvant.

2. Partie expérimentale

On a effectué à 27°C, à l'aide d'un osmomètre Hewlett-Packard modèle 502, des mesures de pression osmotique pour des systèmes binaires polystyrène (PS) — benzène et polyvinylacétate (PVAc) — benzène ainsi que pour des systèmes ternaires PS — PVAc — benzène. On a utilisé quatre fractions de polystyrène standard NBS, monodispersées ($M_w/M_n < 1,1$), ayant les masses molaires : 20 400 ; 37 000 ; 390 000 ; 498 000 et deux échantillons de PVAc obtenus par la fractionnement dans le système acétone — éther de pétrole d'un polyvinylacétate polydispersé BDH, Angleterre. Les échantillons de PVAc utilisés pour cette étude ont eu des masses molaires de 15 400 et 63 400, à un degré d'acétylisation de 100%.

On a utilisé, pour toutes ces déterminations, des membranes confectionnées de la cellulose régénérée, traitées d'après la méthode de Flory-Doust [9], leur réténivité étant testée par des mesures comparatives pour une série d'essais de PS standard à masse molaire comprise entre 10 000 et 670 000 ; pour tous les essais on a obtenu une concordance dans la limite de 1...2% par rapport au masses molaires indiquées de NBS.

La concentration maximum des solutions utilisées pour la détermination du deuxième coefficient du viriel n'a pas dépassée la valeur de 0,01 g/cm³ et dans ce domaine de concentration la rapport π/c varie d'une façon linéaire en fonction de c . Pour obtenir les coefficients de la droite on a utilisé la méthode des moindres carrés.

On a obtenu les systèmes ternaires polymère — polymère — solvant par mélange des solutions des deux polymères. Les mesures osmométriques ont été effectuées après 24...28 heures de la préparation des mélanges.

3. Résultats et discussions

Les valeurs obtenues pour le paramètre d'interaction, χ_{23} , entre PVAc (composant 2) et PS (composant 3) sont représentées, dans la fig. 1, en

fonction du pourcentage gravimétrique de PVAc, pour diverses masses molaires de ces deux polymères.

Pour tous les couples de masses molaires étudiés on constate une diminution du paramètre d'interaction avec l'augmentation du contenu en PVAc, en tendant vers une valeur minimum pour un contenu de 75...85%

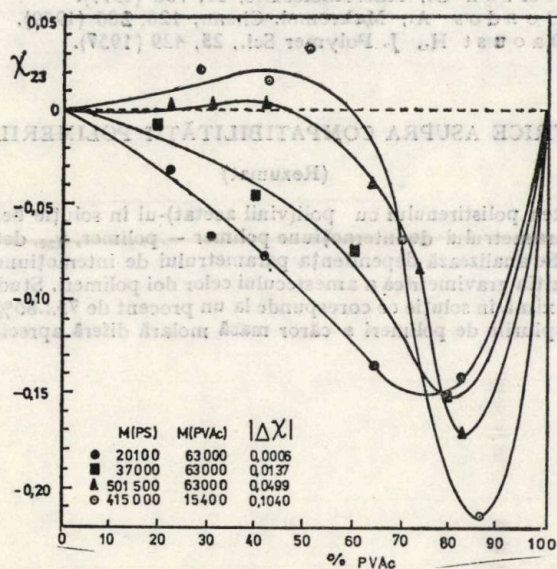


Fig. 1

en poids de PVAc dans le mélange; on peut donc supposer l'existence d'une stabilité maximum des solutions respectives. Toutefois on peut tirer des conclusions que le domaine de compatibilité en solution devient étroit avec l'augmentation des masses molaires des composants polymériques, mais les valeurs χ_{23} négatives, qui indiquent la compatibilité en solution, sont plus prononcées lorsque la différence entre les paramètres d'interaction polymère-solvant (χ_{12} et χ_{13}), dans le domaine de stabilité maximum, est grande.

Par suite, on peut remarquer qu'en général „l'effet $|\Delta\chi|$ “ est respecté, c'est-à-dire que la compatibilité en solution décroît avec l'augmentation des valeurs de $|\Delta\chi|$, à l'exception du domaine de compatibilité maximum ce qui suggère que d'autres effets dans le domaine de la compatibilité maximum en solution des composants doivent exister.

Il est intéressant à remarquer que cette compatibilité maximum suggère un rapport optimum des groupes fonctionnels acétate/styrène de 5:1, pour n'importe quelles valeurs des masses molaires des composants du mélange.

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STUDII OSMOMETRICE ASUPRA COMPATIBILITĂȚII POLIMERILOR ÎN SOLUȚIE

(Rezumat)

Compatibilitatea polistirenului cu poli(vinil acetat)-ul în soluție benzenică diluată este discutată pe baza parametrului de interacțiune polimer - polimer, χ_{23} , determinat prin măsurători osmometrice. Se analizează dependența parametrului de interacțiune de masa molară a polimerilor și compoziția gravimetrică a amestecului celor doi polimeri. Studiul pune în evidență o compatibilitate maximă în soluție ce corespunde la un procent de 75...85% poli(vinil acetat), în special pentru cuplurile de polimeri a căror masă molară diferă apreciabil.

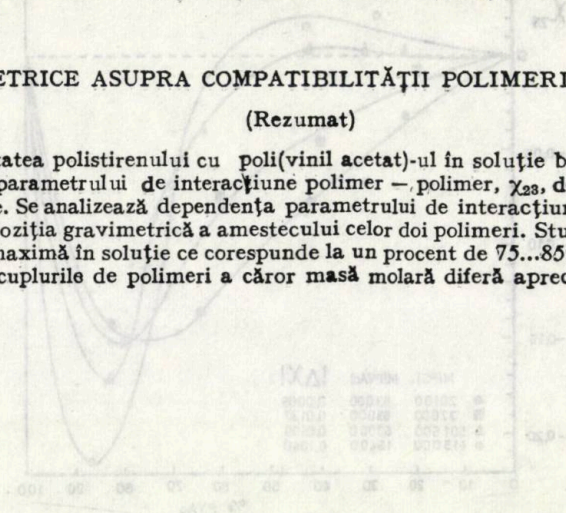


Fig. 1

ÉTUDE SUR LA COMPATIBILITÉ DU SYSTÈME POLYPROPILÈNE— COPOLYMÈRE ÉTHYLÈNE MALÉATE DE BUTYLE

PAR

DOMNICA FURNICĂ, M. FURNICĂ, V. MACOVEI, MĂRIOARA LUCHIAN
et ELENA MIHAI

1. Introduction

La constante préoccupation du perfectionnement des propriétés des matériaux plastiques a donné naissance, en dehors des synthèses de nouveaux polymères et copolymères, à la production de certains alliages de polymères ayant des propriétés différentes de celles des produits d'origine. Dans le cas des alliages de polymères, contrairement à ce qui se passe chez les alliages métalliques, au lieu d'obtenir des systèmes homogènes, on obtient d'habitude la dispersion d'un des polymères dans l'autre et cela, comme résultat des dimensions des macromolécules. Les études effectuées sur un grand nombre de mélanges de composés macromoléculaires ont prouvé que l'incompatibilité est de règle presque générale tandis que la compatibilité représente seulement des cas d'exception [1]. Cependant grâce à la mobilité très réduite des macromolécules à l'état solide, la séparation des réactants d'un mélange de polymères découle très lentement, et par conséquent on peut considérer qu'il s'agit là d'une compatibilité cinétique ou pratique. La durée de stabilité des alliages de polymères est une stricte conséquence de cette compatibilité cinétique qui à son tour paraît être due au degré de dispersion et à la nature des forces d'interaction au niveau des surfaces de séparation des particules finement dispersées. Plus le degré de dispersion est plus avancé et plus les forces d'interaction aux niveaux des surfaces de séparation sont plus fortes, plus la durée de la stabilité et les propriétés physico-mécaniques des alliages de polymères seront améliorées. Dans la réalisation de la pseudocompatibilité, un rôle important revient aux mélanges des composants.

Le rôle de ce travail a été d'établir les limites optima du rapport des composants du mélange en but de réaliser une pseudocompatibilité avancée dans le système polypropylène (PP)—copolymère éthylène maléat de butyle (EMB).

2. Partie expérimentale

Compte tenu de la complexité du phénomène de séparation de phases dans les alliages de polymères on se rend compte que les conclusions relatives données par une seule méthode d'investigation peuvent être considérées comme incomplètes. Par conséquent on a utilisé quatre méthodes d'investigation à savoir : la thermogravimétrie, la séparation des phases dans un solvant commun, la microscopie optique et la spectrophotométrie IR.

On a examiné des mélanges ayant les compositions suivantes : 95 ; 90 ; 85 ; 75 ; 70 et 50% PP et respectivement 5 ; 10 ; 15 ; 20 ; 25 ; 30 et 50%

EMB, obtenues par le procédé du mélange en phase liquide [2]. Les solutions initiales ont eu une concentration de 2 g polymère/100 ml *o*-xylène.

2.1. Étude thermogravimétrique

On a utilisé des pellicules d'alliages polymères obtenues dans un solvant commun (*o*-xylène). Les expériences ont été effectuées dans l'air et dans des conditions dynamiques de température, à une vitesse d'échauffement de 12,8°C/min.; on s'est servi d'un dérivatographe MOM-Budapest, à enregistrement concomitante des courbes TG, DTG et DTA. Chaque échantillon soumis à la décomposition thermique pesait 20 mg.

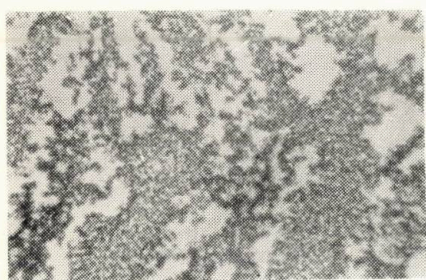
Les dérivatogrammes enregistrés suggèrent une grande complexité DTG du processus de dégradation illustrée surtout dans les courbes (Fig. 1).

Une analyse détaillée de ces courbes suggère des variations spécifiques. En unissant les points qui correspondent au maximum de vitesse de réaction (courbe pointillée, Fig. 1), on observe que la composition de ce maximum, pour le mélange à 20% EMB, diffère des autres. Toutefois en poursuivant la relation entre la variation de la température qui correspond au domaine de la fusion, $t_{fus.}$, mise en évidence par un pic de DTA endotherme et de la température qui correspond au maximum de DTA exotherme, $t_{max.}^{exo.}$, caractéristique pour le processus de dégradation dans l'air et aussi la différence de température des deux pics, donnée dans le tableau 1, on constate un comportement particulier pour le mélange à 20% EMB, surtout en ce qui concerne les valeurs de la température t .

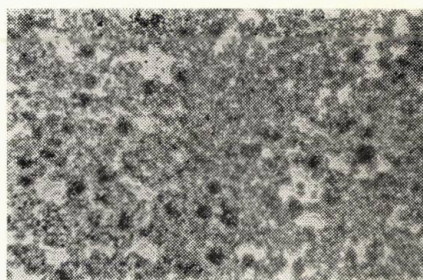
On a calculé aussi l'énergie apparente d'activation caractéristique à la période initiale de dégradation, d'après la méthode Freeman - Carroll [3].

Tableau 1
Valeurs des températures de fusion et des températures qui correspondent aux valeurs maxima du pic DTA exotherme pour des différents mélanges PP-EMB

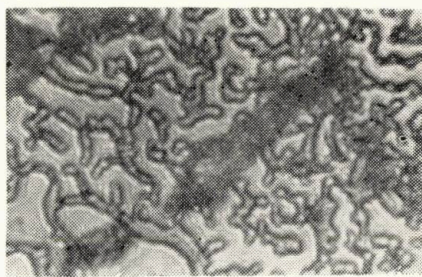
Composition du mélange % EMB	$t_{fus.}$ °C	$t_{max.}^{exo.}$ °C	t °C
5	164	290	126
10	158	312	107
15	163	384	121
20	167	270	103
25	160	313	153
30	165	303	138



a



b



c

Fig. 3. — Les photos des mélanges de PP et EMB dans les proportions : *a* — 85% PP et 15% EMB ; *b* — 80% PP et 20% EMB ; *c* — 75% PP et 25% EMB.



Avec les valeurs obtenues on a construit le diagramme de compatibilité représenté dans la Fig. 2.

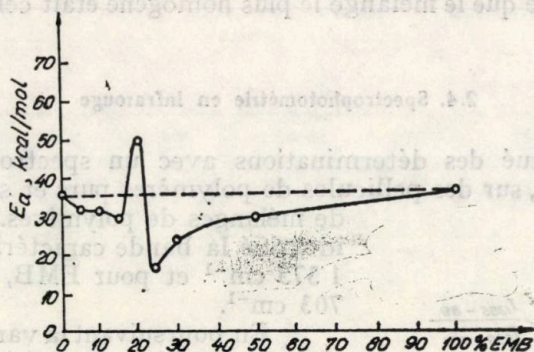


Fig. 2.—Variation de l'énergie apparente d'activation avec la composition des mélanges PP-EMB.

On constate que l'écartement maximum apparaît dans le cas du mélange à 20% EMB.

2.2. Séparation des phases dans un solvant commun

On a effectué la séparation de phases dans un solvant commun dans des cylindres gradués de 100 ml chacun, à bouchon rodé. Les solutions de mélanges des polymères, obtenues conformément au tableau 2, ont été maintenues pendant 24 heures à la température de 116° ... 120°C, dans une étuve thermostable, puis on les a refroidies jusqu'à 90°C. On constate que pour tous les cas, deux phases se sont restées uniformes, en suggérant par cette voie une compatibilité des composants.

Tableau 2

Composition des mélanges de PP-EMB analysés par l'étude de la séparation de phases

Sol. 2% PP ml	Sol. 2% EMB ml	EMB % grav.	Observations
47,5	2,5	5	Séparation de phases
45	5	10	Séparation de phases
42,5	7,5	15	Séparation de phases
40	10	20	Compatibilité
37,5	12,5	25	Séparation de phases
35	15	30	Séparation de phases
25	25	50	Séparation de phases

2.3. Microscopie optique

L'étude microscopique a été effectuée sur des mélanges de polymères sous forme de pellicules, sur des lamelles microscopiques, en se servant d'un

microscope IORMC-1. Les images ont été photographiées avec une exposition de 6 sec., réalisant un agrandissement de 400 fois. En étudiant les photographies on a constaté que le mélange le plus homogène était celui de 20% EMB (Fig. 3).

2.4. Spectrophotométrie en infrarouge

On a effectué des déterminations avec un spectrophotomètre IR, Perkin-Elmer 337, sur des pellicules de polymères purs et sur des pellicules de mélanges de polymères. Pour PP on a identifié la bande caractéristique $1\,370 \dots 1\,375 \text{ cm}^{-1}$ et pour EMB, celle de $699 \dots 703 \text{ cm}^{-1}$.

En poursuivant la variation de l'intensité des bandes caractéristiques des mélanges de polymères, on constate un écart plus grand par rapport à la variation normale de la part du mélange à 20% EMB qui suggère l'existence des forces d'interaction entre les composants du mélange de PP avec EMB (Fig. 4).

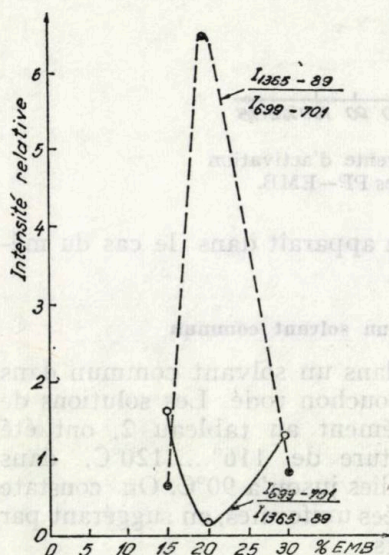


Fig. 4. — Variation de l'intensité relative des bandes d'absorption en fonction de la composition des mélanges de PP et EMB.

3. Conclusions

On a étudié la compatibilité de quelques mélanges de polypropylène avec le copolymère éthylène maleat de butyle par plusieurs méthodes, à savoir : la thermogravimétrie, la séparation de phases dans un dissolvant commun, la microscopie optique et la spectrophotométrie en infrarouge.

En se basant sur les données obtenues on apprécie que le mélange avec 80% PP et 20% EMB présente une pseudocompatibilité maximum.

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STUDIUL COMPATIBILITĂȚII SISTEMULUI POLIPROPILENĂ – COPOLIMER ETILEN MALEAT DE BUTIL

(Rezumat)

Se studiază o serie de amestecuri formate din polipropilenă și copolimerul etilen maleat de butil cu metodele termogravimetrică, separare de faze în solvent comun, microscopie optică și spectrofotometrie în infraroșu. Pe baza datelor obținute se apreciază că amestecul cu 80% PP și 20% EMB prezintă o pseudocompatibilitate maximă.

QUELQUES ASPECTS CONCERNANT LA DÉGRADATION PHOTOCHEMIQUE DES FILMS DE POLYCHLORURE DE VINYLE

II. ÉTUDES THERMOGRAVIMÉTRIQUES

PAR

LUCIA ODOCHIAN, CORNELIA VASILE et MĂRIOARA LUCHIAN

1. Introduction

Dans un travail antérieur [1] on a étudié les modifications de poids moléculaire, de structure et de l'aspect microscopique des films de polychlorure de vinyle sous l'action des radiations UV, associées avec les conditions de pluie.

On a montré que, après l'exposition, croît la polydispersion par rapport à la masse moléculaire de l'échantillon, quelques films se sont opacifiés grâce à l'hétérogénéité de la surface et en même temps apparaissent des groupes peroxydiques, qui ultérieurement conduisent à la diminution de la stabilité du polymère due à l'initiation plus facile des réactions d'oxydation.

Afin d'apporter des preuves supplémentaires concernant ce dernier aspect on a effectué une étude du comportement thermique des échantillons non-exposés et exposés aux radiations UV.

2. Partie expérimentale

Les échantillons étudiés et les conditions d'expositions sont identiques avec celles utilisées dans la Note précédente [1].

Les études de décomposition thermooxydative ont été effectuées à l'aide d'un dérivatographe MOM-Budapest, type Paulik-Paulik-Erdey, en utilisant une vitesse de chauffage de $12,4^{\circ}\text{C}/\text{min}$. Le poids des échantillons a été de 15 mg, la grosseur des films $8\ldots 10\ \mu$ et on a utilisé comme matériel de référence Al_2O_3 frais calciné.

On a déterminé tant les températures caractéristiques et les pertes en poids, que la variation des paramètres cinétiques après l'exposition.

Les énergies d'activation ont été évaluées par les méthodes Freeman-Carroll [2] et Reich-Levi [3] en utilisant des programmes de calcul écrits en FORTRAN IV [4].

Les résultats présentés représentent la moyenne de 4 ... 5 déterminations.

3. Résultats et discussion

Les courbes DTG et DTA, représentées dans les Fig. 1 et 2, mettent en évidence une complication du processus de décomposition des échantillons

exposés. Dans les deux types de courbes il y a un nombre plus grand d'étapes de décomposition tandis que le caractère exotherme des processus mis en évidence dans les courbes DTA, qui se déroulent après la réaction de dehydrochloruration, est accentué. En même temps on observe un dépla-

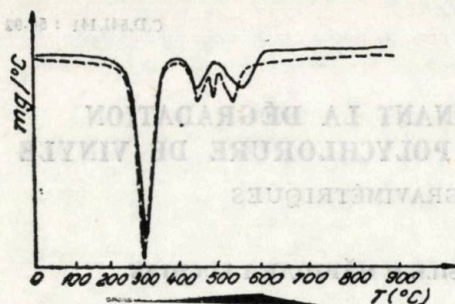


Fig. 1. — Les courbes DTG d'une pellicule de PVC initiale (—) et exposée aux radiations UV (---).

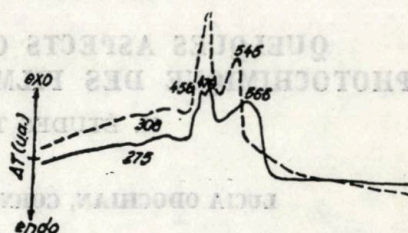


Fig. 2. — Les courbes DTA d'une pellicule de PVC initiale (—) et exposée aux radiations UV (---).

cement des sommets caractéristiques pour différentes étapes de décomposition ainsi comme il résulte si l'on analyse les valeurs concentrées dans le tableau 1.

Tableau 1

Les grandeurs caractéristiques dans les courbes DTG, DTA et TG pour les échantillons exposés et non-exposés

	Nr. des étapes	Les échantillons	
		non-exposés	exposés
Températures caractéristiques dans les courbes DTG, [°C]	I	188	184
		308	304
		384	398
	II	412	418
T_i T_m T_f	III	452	459
		496	489
		496	438
	IV	562	496
		612	512
		—	512
Température du sommet DTA T_m , [°C]	I endotherme	—	550
	II exotherme	—	709
	III exotherme	307	304
Les pertes en poids, [%], courbe (TG)	I	488	474
	II	546	551
	III	61,5	58,5
La perte totale	III	11,7	13,16
		17,7	18,4
		84,97	90,13
Le résidu		15,03	9,87
La surface des sommets exothermiques (II + III), [cm ²]		5,60	6,46

T_i — température initiale; T_m — température qui correspond à la vitesse maximum de décomposition; T_f — température finale de décomposition.

En réalité il y a deux effets contraires, comme on peut constater si l'on analyse les déterminations des poids moléculaires. Au début, dans la première étape de décomposition, les températures caractéristiques des courbes DTG indiquent une diminution de la stabilité thermique et après l'exposition les températures initiales sont plus basses. Pour les étapes suivantes les températures caractéristiques pour les échantillons exposés sont plus élevées, probablement à cause des réticulations présentes dans le film. Une même constatation est mise en évidence si l'on compare les températures caractéristiques des courbes DTA.

Une explication des ces modifications est possible par l'examen des variations des pertes en poids pour la première étape de décomposition, celles-ci étant plus petites dans le cas des échantillons exposés. La diminution de la perte en poids pour la première étape s'explique par l'élimination d'une quantité d'ingrédients au cours de l'exposition, ainsi comme il résulte des données fournies par le tableau 2.

Tableau 2

La modification de la composition des films PVC après l'exposition

		Non-exposés	Exposés
I.	Analyse élémentaire : Cl, [%] ;	38,14	41,035
	PVC, [%] ;	67,14	72,24
	Ingrédients, [%]	32,86	27,76
II.	Spectroscopie UV : PVC [%] ;	71,50	75,60
	Ingrédients, [%]	28,50	24,40
III.	Déterminations gravimétriques : PVC [%] ;	72,92	77,52
	Ingrédients, [%]	27,08	22,48

Dans la deuxième étape de décomposition les pertes en poids sont plus grandes, de même que la perte totale. En même temps diminue la quantité de résidu. Il résulte que, comme conséquence de l'apparition des groupes peroxydiques pendant l'exposition sont favorisées les réactions de scission et d'oxydation. Le caractère prépondérant du dernier type de réaction peut être remarqué également par l'augmentation de la surface totale des „peaks“ exothermiques DTA.

L'abaissement de la quantité de résidu peut être considérée comme conséquence du fait que les réactions de scission sont plus fréquentes que celles de cyclisation de la structure polyennique qui se manifestent après la dehydrochloruration.

L'existence de ces deux effets compétitifs (oxydation et réticulation), qui se manifestent après l'exposition aux radiations UV, est bien mise en évidence aussi par la variation des valeurs des paramètres cinétiques présentées dans les Fig. 3 et 4.

Par les deux méthodes de calcul utilisées, Freeman-Carroll (Fig. 3) et Reich-Levi (Fig. 4), on trouve que pour les premières étapes (un degré de transformation de 5 ... 6%) de la réaction de décomposition,

les valeurs de l'énergie apparente d'activation pour l'échantillon exposé sont plus petites que celles qui correspondent à l'échantillon initial, respectivement 79,5 KJ/mol par rapport à 122 KJ/mol ; pour les étapes ultérieures le rapport s'inverse (91,79 KJ/mol pour l'échantillon initial et 110,93 KJ/mol pour celui exposé) comme conséquence de l'intensification de l'influence des ramifications et des réactions de réticulation [5].

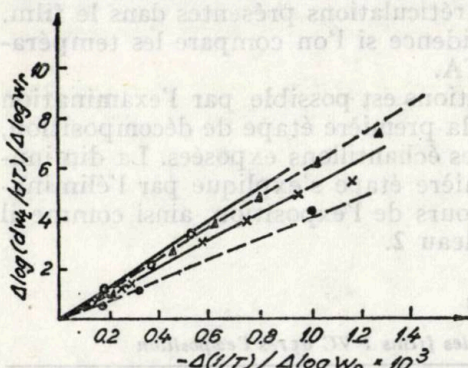


Fig. 3. — Le diagramme Freeman-Carroll pour un échantillon de PVC initial (—) et exposé aux radiations UV (---) ; pertes en poids 0...7% (○, ●) ; 7...50% (×, Δ).

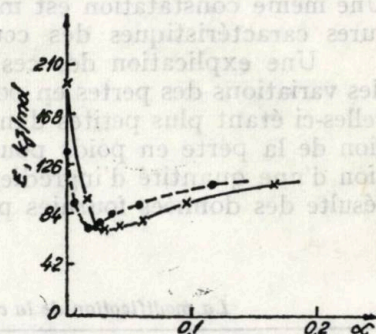


Fig. 4. — La variation de l'énergie d'activation, E_a , en fonction du degré de transformation pour un film de PVC initial (—) et exposé aux radiations UV (---).

3. Conclusions

Les résultats obtenus permettent à aboutir à la conclusion que par l'exposition des films de polychlorure de vinyle aux radiations UV, l'apparition des groupes peroxydiques conduit au processus de vieillissement du polymère, accompagné de la diminution de la stabilité thermique.

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UNELE ASPECTE ALE DEGRADĂRII FOTOCHIMICE A FILMELOR DE POLICLORURĂ DE VINIL

II. Studii termogravimetrice

(Rezumat)

S-a studiat, pe cale termogravimetrică, comportarea termică a filmelor de policlorură de vinil neexpuse și expuse la radiații UV, asociate cu ploaie.

Rezultatele obținute au condus la concluzia că îmbătrânirea polimerului este însoțită de scăderea stabilității termice.

ALKYLATION OF TOLUENE WITH METHANOL ON SYNTHETIC ZEOLITES

IV. STATISTICAL-MATHEMATICAL ANALYSIS OF THE PROPERTIES, STRUCTURAL CHARACTERISTICS OF CATALYSTS AND REACTION TEMPERATURE INFLUENCE ON CATALYTICAL ACTIVITY

BY

N. NAUM, FLORIN VITAN, GH. MIHĂILĂ, GH. SURPĂȚEANU and V. ABABI

1. Introduction

The cumulative influence of the zeolite catalytical properties [1]...[5] and their main structural factors that determines the catalyst surface acidity [6], [7], as well as of the chemical nature factors, such as dicationization degree [8] and the nature of the exchanging ions [9], explain the complex aspects that characterizes the existence of the acidity forms on the zeolite catalysts surface.

Taking into account that, depending on the activation temperature of catalysts and operating temperature [10]...[12], besides the alkylation reaction there are taking place other reactions such as isomerization, disproportionation and dimethylation, in order to establish the conditions under which the selective obtention of the single alkylate products is favoured, as well as to minimize the experiments number, earlier, a theoretical study of toluene alkylation with methanol has been carried out [13]...[15].

In some previous papers [16], [17] there was investigated the influence of acid properties of zeolites containing rare earth, as well as the operating temperature, over the catalytical activity.

The present paper deals with a statistical-mathematical analysis of the above mentioned parameters on catalytical activity of some synthetic zeolites tested on toluene alkylation with methanol.

2. Analysis of the Experimental Data

The experimental data have been obtained using a laboratory plant, described in a previous paper [17]. By manner of the experimental part presentation, this can be assumed to be of „Black box“ type, in which the inputs are operating temperature T , molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$, symbolized by X and catalyst type, symbolized by C . The outputs are represented by the molar fraction of p -, m - and o -xylene in the obtained aromatic hydrocarbons mixture. The experimental program has been elaborated on the basis of the upper order factorial experiments, which shows the minimum experiments number necessary to establish the conclusions as regards the influence of the controlling factors on the outputs.

During the experimentation, there were taken five levels for temperature, two levels for molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$, and two levels for the catalyst type. The experimental results are summarized in Table 1.

Table 1

Composition of the Xylenes Mixture Obtained on Faujazitc Catalysts

	$X_1 = 4.25$					
	$C_1(\text{CeY})$			$C_2(\text{LaY})$		
	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene
$T_1=180^\circ\text{C}$	20.00	6.50	73.50	18.50	5.80	75.70
$T_2=200^\circ\text{C}$	31.76	29.82	38.42	29.57	27.44	42.99
$T_3=220^\circ\text{C}$	36.27	32.65	31.08	34.37	31.89	30.26
$T_4=240^\circ\text{C}$	31.73	37.15	29.02	28.79	41.71	29.50
$T_5=260^\circ\text{C}$	26.77	43.58	29.65	23.25	48.15	28.60
	$X_2 = 5.36$					
	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene
	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene
$T_1=180^\circ\text{C}$	33.14	11.60	55.26	28.14	9.94	61.92
$T_2=200^\circ\text{C}$	43.96	21.05	34.99	41.05	25.37	33.58
$T_3=220^\circ\text{C}$	46.83	30.92	22.25	44.51	29.66	25.83
$T_4=240^\circ\text{C}$	41.96	37.96	20.08	39.98	35.27	25.75
$T_5=260^\circ\text{C}$	36.54	45.67	17.79	35.09	40.89	24.02

The statistical analysis of the results concentrated in Table 1 was effected on the basis of an algorithm for the upper order factorial experiments. This way requires to decompose the Table 1 in three tables with two levels each, by successive elimination of a factor, summing the values determined on outputs for each level of respective factor [18], [19]. The partial values obtained by this procedure are presented in the Tables 2 ... 4.

Table 2

Partial Table CX, with Two Factors

	X_1			X_2			Total		
	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene
C_1	146.53	149.7	201.67	202.43	147.2	150.37	348.96	296.90	352.04
C_2	134.48	154.99	207.05	187.77	141.13	171.10	322.25	296.12	378.15
Total	281.01	304.69	408.72	390.20	288.33	321.47	671.21	593.02	730.19

Using the data from Tables 2 ... 4, the dispersion due to the chosen factors and their interaction, as well as the residual dispersion, necessary for dispersional analysis, have been calculated.

Table 3

Partial Table CT. with Two Factors

C	T. 1			T. 2			T. 3			T. 4			T. 5			Total		
	p-xylene	m-xylene	o-xylene	p-xylene	m-xylene	o-xylene	p-xylene	m-xylene	o-xylene	p-xylene	m-xylene	o-xylene	p-xylene	m-xylene	o-xylene	p-xylene	m-xylene	o-xylene
C. 1	53.14	18.10	128.76	75.72	50.87	73.41	83.10	63.57	53.33	73.69	75.11	49.10	63.31	89.25	47.44	348.96	296.90	352.04
C. 2	46.64	15.74	137.62	70.62	52.81	76.57	78.88	61.55	56.09	67.77	76.98	55.25	58.34	89.04	52.62	322.25	296.12	378.15
Total	99.78	33.84	266.38	146.34	103.68	149.98	161.98	125.12	109.42	141.46	152.09	104.35	121.65	178.29	100.06	671.21	593.02	730.19

Table 4

Partial Table XT, with Two Factors

X	T. 1			T. 2			T. 3			T. 4			T. 5			Total		
	p-xylene	m-xylene	o-xylene	p-xylene	m-xylene	o-xylene	p-xylene	m-xylene	o-xylene	p-xylene	m-xylene	o-xylene	p-xylene	m-xylene	o-xylene	p-xylene	m-xylene	o-xylene
X. 1	38.50	12.30	149.2	61.33	57.26	81.41	70.64	64.54	61.34	60.52	78.86	58.52	50.02	91.73	58.25	281.01	304.69	321.72
X. 2	61.28	21.54	117.18	85.01	46.42	68.57	91.34	60.58	48.08	80.94	73.23	45.83	71.63	86.56	41.81	390.20	288.33	321.47
Total	99.78	33.84	266.38	146.34	103.68	149.98	161.98	125.12	109.42	141.46	152.09	104.35	121.65	178.29	100.06	671.20	593.22	730.19

Table 5

Dispersional Analysis

Dispersion source		Nr. of freedom degrees	Dispersion S^2			$F = S^2/S_r^2$			$F_{0.05}$ $F_{0.01}$
			<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene	
Between columns	<i>C</i>	1	35.671	0.03	34.086	35.958	0.00299	5.0589	7.71 21.20
	<i>X</i>	1	596.123	13.383	380.628	600.93	1.3363	56.491	7.71 21.20
	<i>T</i>	4	144.628	758.36	1 230.65	145.794	75.724	182.650	6.39 15.98
Between rows	<i>CX</i>	1	0.341	6.452	11.782	0.3437	0.6442	1.7486	7.71 21.20
	<i>CT</i>	4	0.1957	1.0522	1.5265	0.1973	0.1050	0.2265	6.39 15.98
	<i>XT</i>	4	0.4772	13.9662	17.173	0.4810	1.3945	2.5488	6.39 15.98
Residual		4	0.992	10.0147	6.7377	—	—	—	—

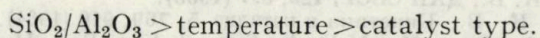
To establish the freedom degrees for dispersion calculation, it was taken into account that in the partial table *CX*, the eliminated factor, *T*, was in Table 1 on five levels and the factor *X*, eliminated in the partial table *CT*, was in the Table 1 on two levels and, finally, the factor *C*, eliminated in the partial table *XT*, was in Table 1 on two levels too.

Dispersion of the factors and the dispersion due to their interaction reported to the residual dispersion was noted by *F*. The value of *F* was compared with critical values of Fischer's distribution F_α , for the significance threshold α equal to 0.05 and 0.01.

Results of the dispersional analysis are summarized in Table 5.

3. Discussion

Comparison of *F* with F_α in Table 5 points out that the variation of temperature reaction, molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ and catalyst type, influences significantly concentration of *p*-xylene in the reaction product for 99% cases. Influence of the three factors is situated in the order:



Concentration of *m*-xylene is influenced by reaction temperature only, and concentration of *o*-xylene is influenced for 99% cases by the molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ and reaction temperature, latter having higher influence than former.

As it also comes out from Table 5 the effect of interaction between factors, for both significance thresholds, is not significantly. On the other words, no matter which of them influences on concentration of *p*-xylene, independently by the level on which there are the other two factors. Concen-

tration of *m*-xylene is influenced by reaction temperature only, independently of the level where are the two factors; the concentration of *o*-xylene is influenced by the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ and the reaction temperature, and is not influenced by the level of the other factor.

Taking into account these conclusions and analysing the results concentrated in Table 1, in order to get maximum *p*-xylene concentration the alkylation must be performed under the following conditions: reaction temperature 220°C (T_3), catalyst CeY (C_1) and molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ equal to 5.36 (X_3). Under these conditions, xylenes concentration is 46.83, 30.92 and 22.25% for *p*-xylene, *m*-xylene and *o*-xylene, respectively.

Concentration of *m*-xylene increases as reaction temperature becomes higher and concentration of *o*-xylene decreases as reaction temperature and molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ become higher.

4. Conclusions

Statistical analysis of the experimental data as regards the toluene alkylation with methanol on synthetic zeolites, based on an algorithm for upper order factorial experiments, pointed out that variation of the reaction temperature, molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ and catalyst type influences differently on xylenes concentration.

In order to get the maximum concentration of *p*-xylene, the following combination of the factors levels must be chosen: reaction temperature, equal to 220°C (T_3), catalyst CeY (C_1) and molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ equal to 5.36 (X_2).

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ALCHILAREA TOLUENULUI CU METANOL PE ZEOLIȚI SINTETICI

IV. Analiza statistico-matematică a influenței proprietăților, caracteristicilor structurale ale catalizatorilor și a temperaturii de reacție asupra activității catalitice

(Rezumat)

Datele experimentale obținute în urma cercetării alchilării toluenului cu metanol, în fază gazoasă, pe catalizatori zeolitici sintetici, au fost supuse analizei statistico-matematice în vederea stabilirii condițiilor optime pentru obținerea randamentului maxim în *p*-xilen. Analiza datelor, pe baza algoritmului pentru experiențe factoriale de ordin superior, a arătat că modificarea temperaturii de reacție, a raportului molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ și a tipului de catalizator, influențează în mod diferit concentrația celor trei xileni din amestecul obținut. Concentrația maximă în *p*-xilen a amestecului se obține dacă se folosește următoarea combinație a nivelelor factorilor considerați: temperatura de reacție de 220°C (T_3), catalizatorul CeY (C_1) și raportul molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ de 5,36 (X_2).

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ALCHIMIA SOLUȚIILOR CU METALOI PE ZBOULI SINTETICI

IV. Analiza statistico-matematică a influenței proprietăților caracteristice ale sistemelor catalitice și a temperaturii de reacție asupra activității catalitice

(Rezumat)

Datele experimentale obținute în urma cercetării stabilirii tehnologiei de producție, în condiții industriale, pe catalizatori sintetici, au fost supuse analizei statistico-matematice în vederea stabilirii condițiilor optime pentru obținerea randamentului maxim în reacția Al₂O₃ + 3H₂ → 2Al + 3H₂O. Pentru aceasta s-a utilizat metoda planului factorial, iar pentru analiza rezultatelor s-a utilizat metoda analizei statistice. În urma analizei s-a constatat că temperatura de reacție are cea mai mare influență asupra randamentului, urmată de concentrația de Al₂O₃ și de timpul de reacție. În funcție de temperatura de reacție s-a determinat concentrația optimă de Al₂O₃ și timpul optim de reacție. Astfel, la 350°C, concentrația optimă de Al₂O₃ este de 2,36 (wt. %).

STUDIES ON THE RHEOLOGICAL BEHAVIOUR OF SOME FERMENTATION BROTHS *)

BY

RADU Z. TUDOSE, ECATERINA MERICĂ, NICULINA TEPORU, IORDAN PAIU,
and C. PONCU

1. Introduction

Fermentation broths of antibiotics are, in general, non-Newtonian; the variation of composition and consistency of the broths during the fermentation course results in changes of the rheological properties.

Engineering design and scale-up of the fermentation processes require knowledge on the rheological properties of the fermentation broths. The rheological data are necessary for designing the appropriate mixers and pipes and for studying the mass and heat transfer processes in commercial fermenters [1], [2].

It was already pointed out [2] that the oxygen transfer during the fermentation is closely related to the rheological behaviour of the broth. Thus, the increase of the mycelial mass results in a significant decrease of the rate of oxygen dissolution. At a concentration of 3% (dried substance) the rate of oxygen dissolution diminishes with 90%.

Under these conditions the mixing is absolutely necessary, influencing in a great extent the broth activity. The power consumption for stirring the broth depends on the microorganism type, but in evaluating the power requirements the broth viscosity and its variation in time or with the shear rate are of primary significance.

One of the most obvious applications based on the knowledge of the rheological behaviour of broths is the characterization of the mycelial growth. Small changes in the concentration of the mycelial mass turns into large changes of the broth fluidity. Since in most cases the fermentation processes proceed in media containing suspended solid materials, which makes difficult the accurate determination of the cellular mass, the following of the latter growth might be accomplished by following the variation of the broth rheological properties. This method proved to be a sensitive analytical mean for detecting the growth of the cellular mass during fermentation.

Though in the field of biochemical process engineering knowledge of the rheological behaviour of the fermentation broths is a problem of high interest the reported papers on this subject are rather few, most of them being published after 1960 [1]...[8].

The rheological behaviour of some fermentation broths as resulted from literature data is given in Table 1.

The fact deserves mention that, excepting nystatin, all the other fermentation broths exhibit non-Newtonian behaviour, generally pseudoplastic, some of them exhibiting also thixotropic.

*) Presented at the National Congress of Chemistry, Bucharest, Sept. 8-10, 1978.

Table 1
Rheological Behaviour of some Fermentation Broths

Fermentation process	Microorganism	Principal nutrient in medium	Rheological behaviour	Reference
Nystatine	<i>Streptomyces</i>	glucose – soya bean meal	Newtonian	[3]
Penicillin	<i>Penicillium chrysogenum</i>	lactose – corn steep liquor	Pseudoplastic	[2], [3], [6]
Kanamycin	<i>Streptomyces kanamyceticus</i>	Starch – soya bean meal	Pseudoplastic and plastic	[2], [3]
Streptomycin	<i>Streptomyces griseus</i>	Soya bean meal – glucose	Thixotropic	[2], [3]
Steroid hydroxylation	<i>Coniothyrium helveticum</i>	Salts – glucose	Plastic and pseudoplastic	[3]

The aim of these paper is to study the change of the rheological properties of some penicillin and streptomycin broths during the fermentation course.

2. Experimental

The measurements were carried out on samples taken at equal time intervals (at every eight hours) during the whole fermentation process.

The measurements were taken on a viscometer with concentric cylinders of the Rheorest 2 type, at 27°C. The samples of 25 ml were kept under stirring to maintain the homogeneity.

The change of the shear stress with the shearing rate was followed at increasing and decreasing shear rates. For every run the corresponding shear stress and viscosity were calculated.

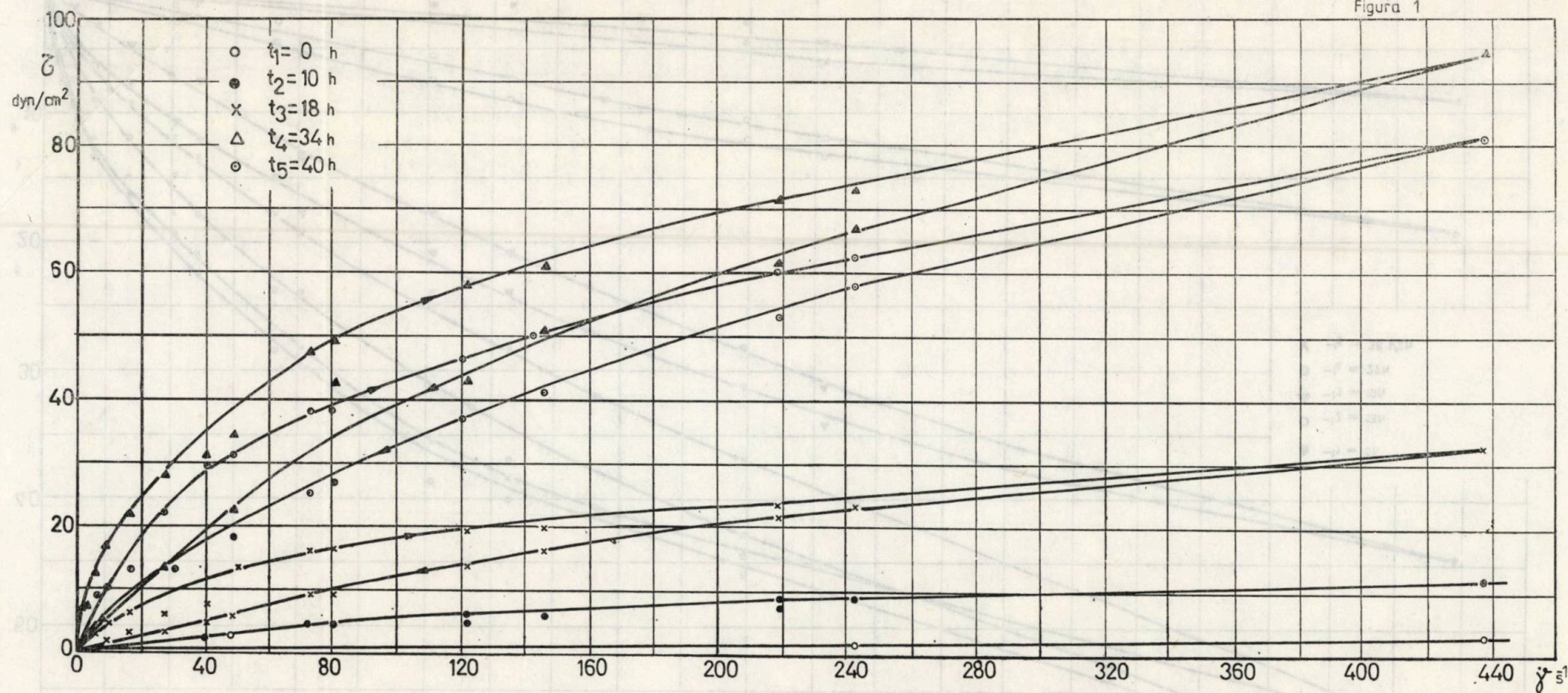
3. Results and Discussion

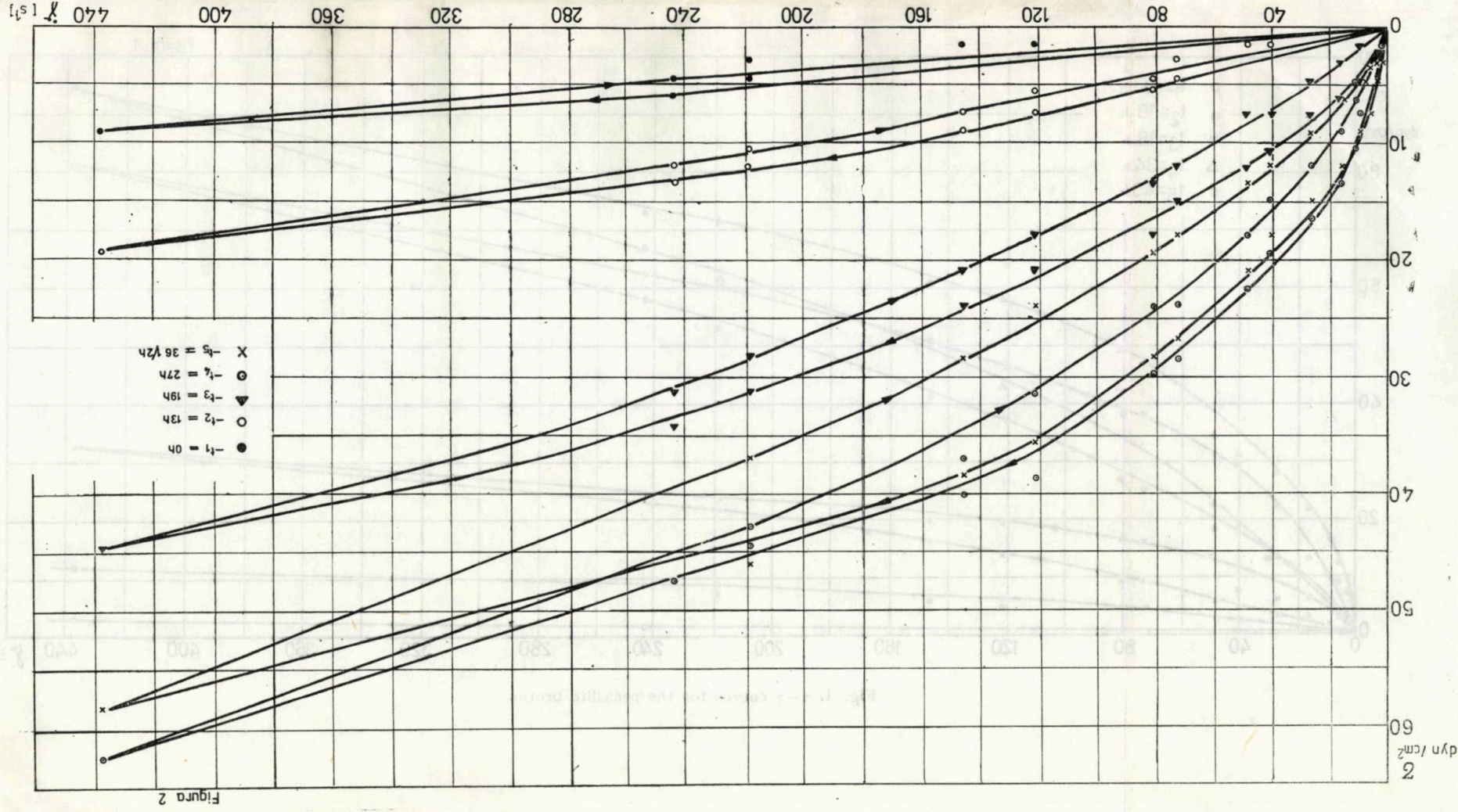
The experimental results obtained have been plotted. By analysing the $\tau-\dot{\gamma}$ diagrams given in Figs. 1 and 2 for penicillin and streptomycin, respectively, a clear thixotropic behaviour is evidenced, resulting in hysteresis loops. Thus, up and down curves were obtained for increasing and decreasing shear rates. Similar results on the fermentation broth thixotropy were also reported by Satoh [2] for the streptomycin and kanamycin broths.

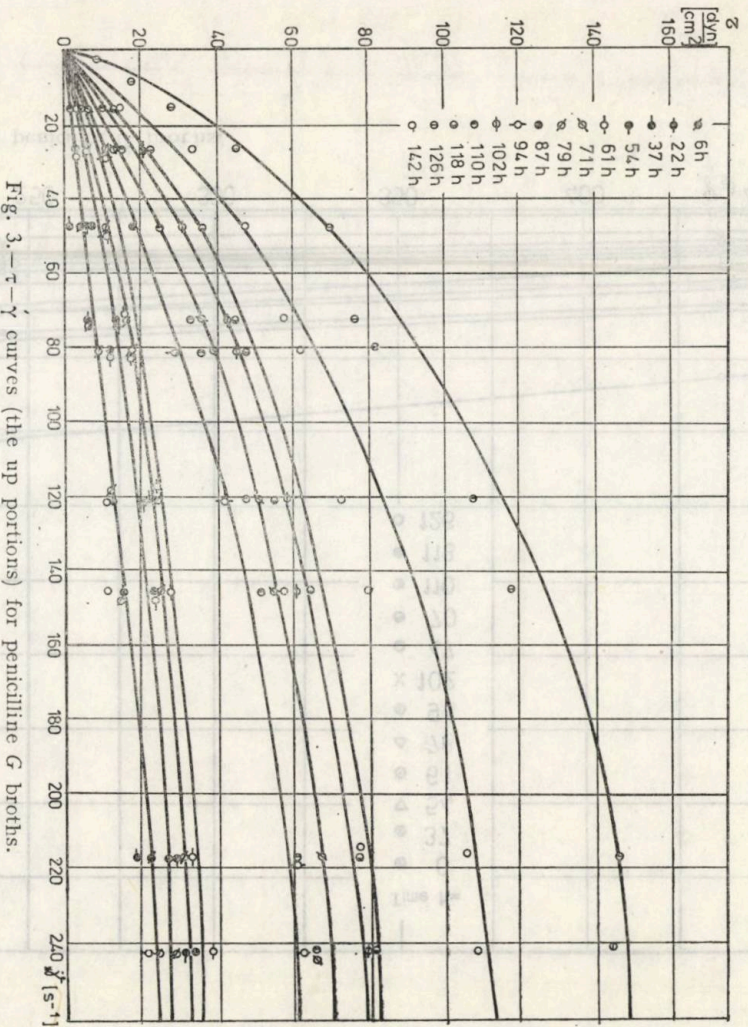
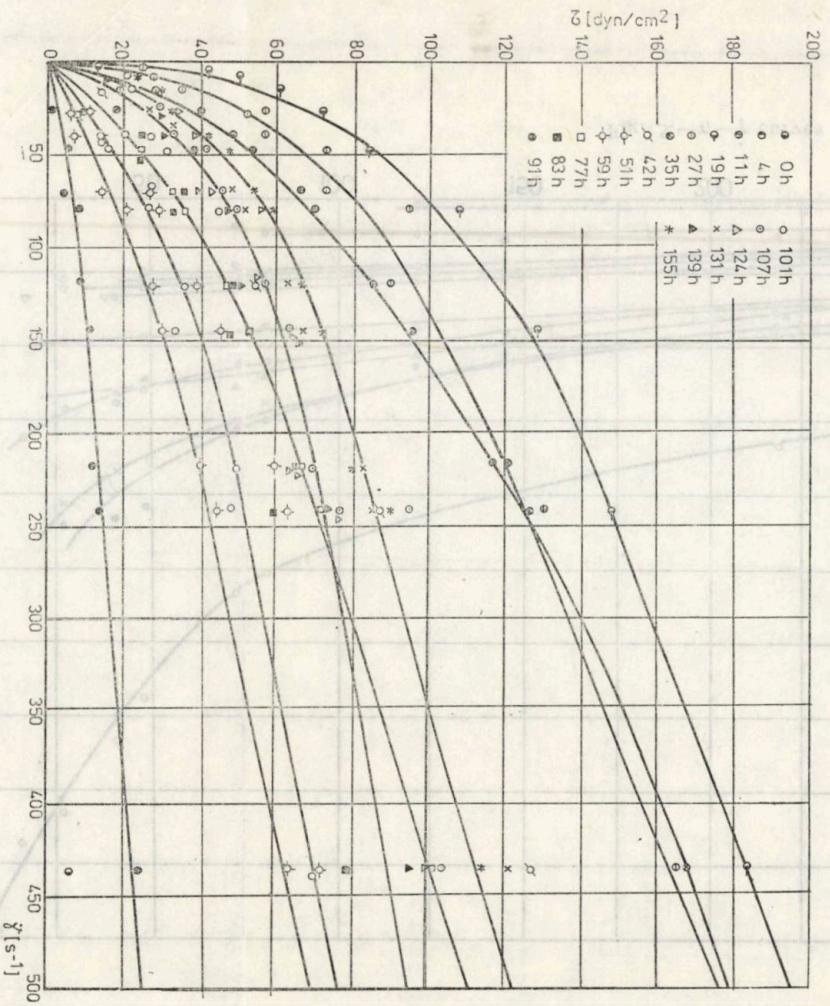
The correlation $\tau-\dot{\gamma}$ for the up curve of the hysteresis loop is given in Figs. 3 and 4, for the same broths as above. The curve features clearly indicate a pseudoplastic behaviour, that is a gradually increase of the shear stress with increasing shear rate followed by a linear relationship settled above a certain value of the shear rate [1].

The change from the nonlinear to the linear relationship is to be noticed at approximately 120 s^{-1} for the penicillin broth and 200 s^{-1} for the streptomycin broth, respectively. This behaviour is characteristic to media suffering a structural alteration during shearing, fact also supported by the existence of hysteresis loops.

Figura 1

Fig. 1. $\tau-\dot{\gamma}$ curves for the penicillin broths.



Fig. 3.— τ - $\dot{\gamma}$ curves (the up portions) for penicilline G broths.Fig. 4.— τ - $\dot{\gamma}$ curves (the up portions) for the streptomycin broths.

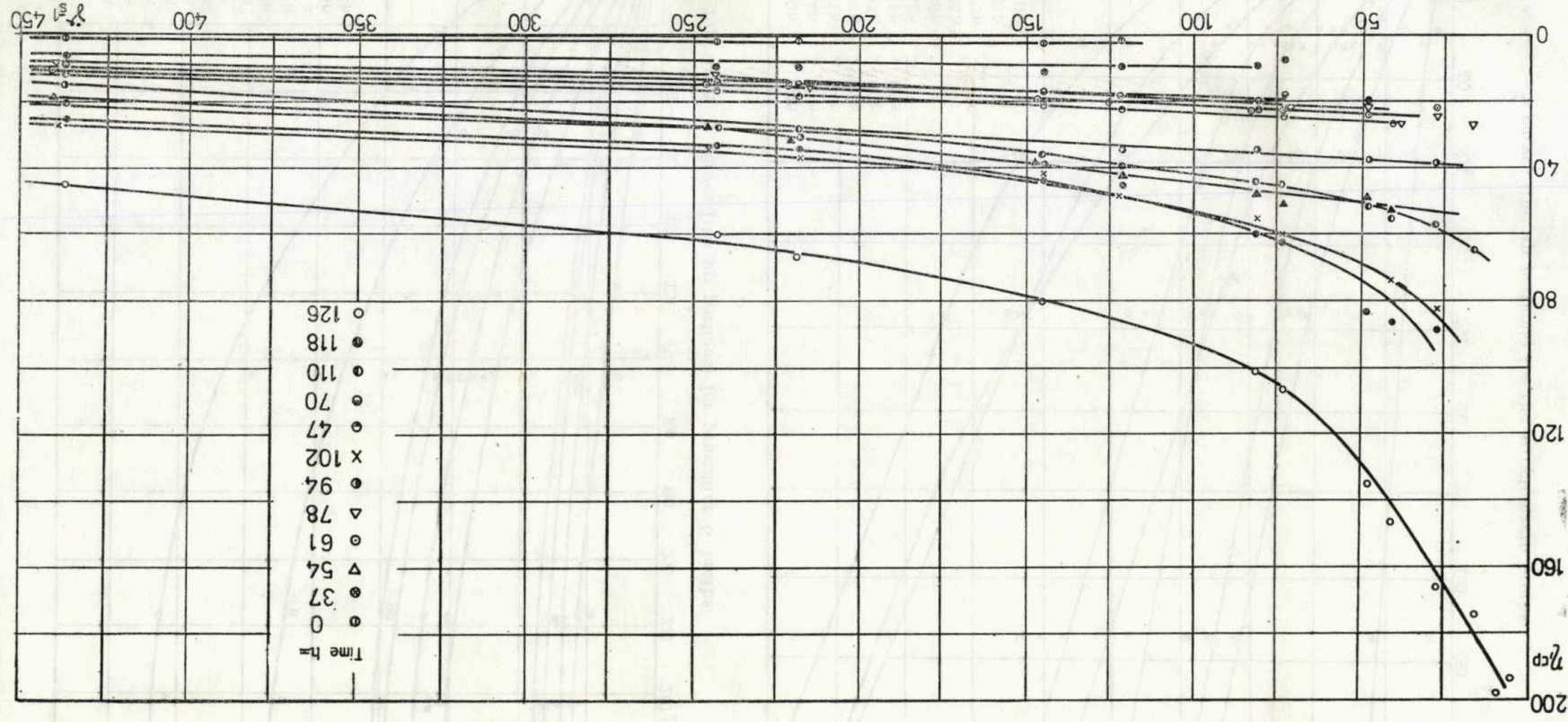


Fig. 5.— η - γ curves for penicillin G broths.

The correlation viscosity—shear rate is represented in Figs. 5 and 6. It is to notice that while the broth viscosity is independent on the shear rate at the process beginning (fermentation time zero), after the fermentation occurrence it decrease with increasing shear rate.

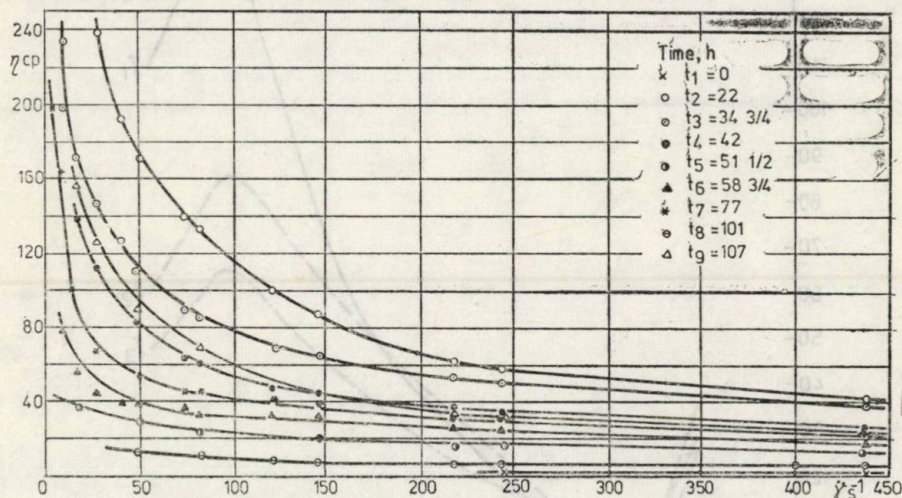


Fig. 6.— η — $\dot{\gamma}$ curves for streptomycin broths.

In Figs. 7 and 8 the curves representing the viscosity variations in time are given for penicillin and streptomycin broths respectively. As can be seen in Fig. 7 the viscosity of the penicillin broth lowers at the beginning (till approximately 40 hours), increases then (till approximately 120 hours) and decreases again. A similar behaviour can be noticed also for streptomycin but the time intervals at which these changes occur are somewhat different.

The explanation of this fact might be found in the correlation between the viscosity change on one hand and the broth composition variation connected with the mycelial growth and nutrient consumption on the other hand. It was already pointed out that the broth viscosity is largely influenced by both nutrient and mycelial concentrations. Thus, the lowering of the nutrient contents during the fermentation results in diminishing the viscosity while the mycelium growth has an opposite effect.

Clearly, as the nutrient is consumed the cellular mass grows, but the correlation growth—consumption is not a simple one. Thus, the viscosity decrease during the first part of the fermentation process might indicate the fact that the mycelial growth does not balance, in effect, the nutrient consumption. Later on, the fast growth of the cellular mass becomes the governing factor in the viscosity increase.

Otherwise, during the fermentation process the form and the dimensions of the cells also modify. Thus, *Penicillium chrysogenum*, producing penicillin, forms at first filamentous mycelium and growth mainly in compact pellet form, developing later in spongy pellet form along the proceeding fermentation. It might be thus supposed that the conformational

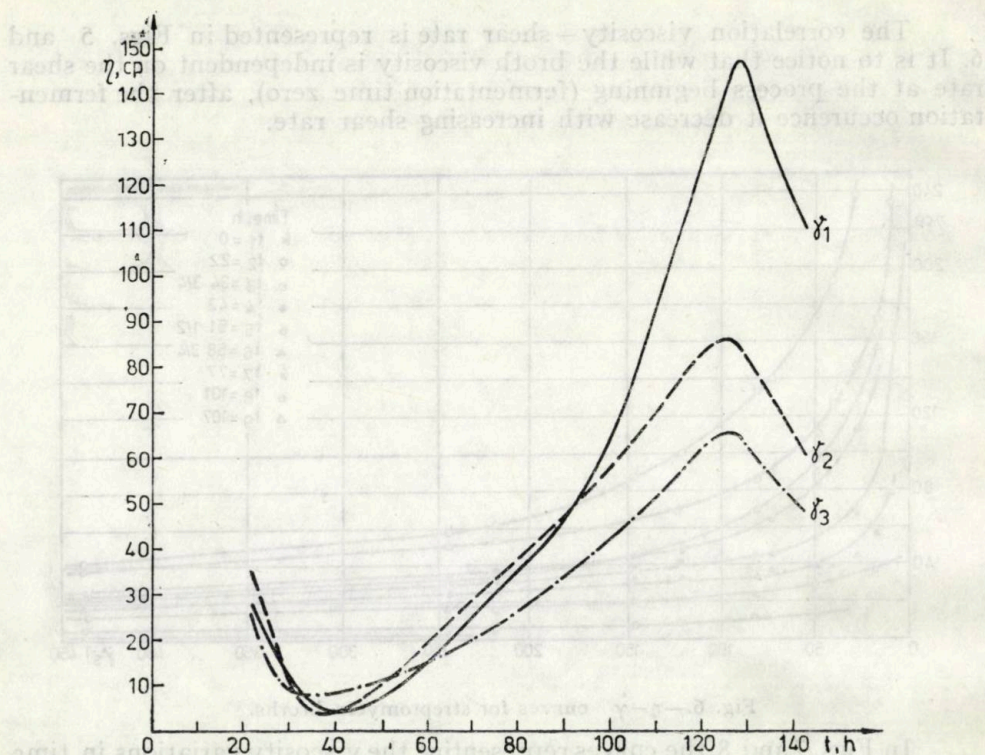


Fig. 7. — Viscosity vs. time curves for the penicillin broth at various shear rates ($\dot{\gamma}_1 = 40 \text{ s}^{-1}$; $\dot{\gamma}_2 = 120 \text{ s}^{-1}$; $\dot{\gamma}_3 = 220 \text{ s}^{-1}$).

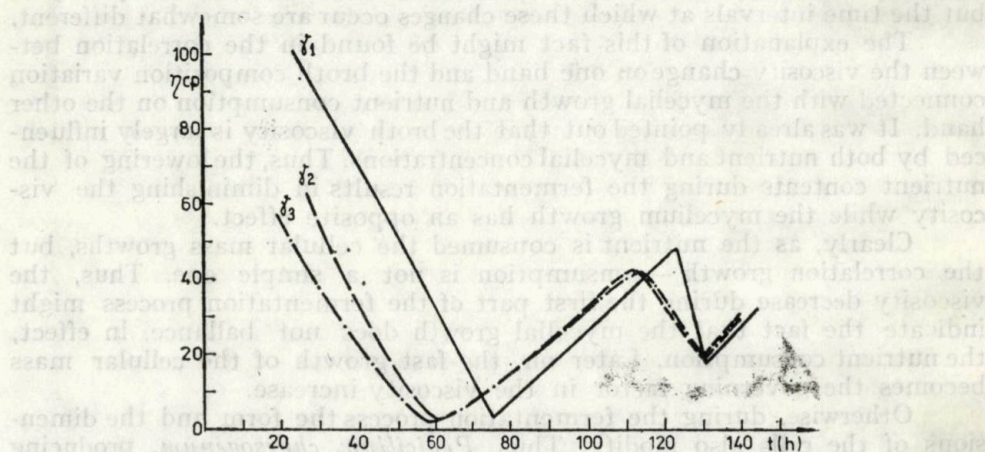


Fig. 8. — Viscosity vs. time curves for the streptomycin broth at various shear rates ($\dot{\gamma}_1 = 40 \text{ s}^{-1}$; $\dot{\gamma}_2 = 120 \text{ s}^{-1}$; $\dot{\gamma}_3 = 220 \text{ s}^{-1}$).

and dimensional changes of the mycelial mass could result in significant changes of the rheological properties of the fermentation broths.

For the up parts of the $\tau-\dot{\gamma}$ curves a modelling of power law type was tried and n and k values calculated for every run. The values of n were found to lie within the following range:

$n=0.90...0.61$ for penicillin, $N=0.835...0.566$ for streptomycin.

4. Conclusions

1. The variation of rheological behaviour of some fermentation broths of penicillin and streptomycin was investigated.
2. The obtained results indicate for both broths a thixotropic behaviour.
3. For the up curves a modelling of the power law type was tried, the values of n and k being determined for every run.
4. The curves of broth viscosity change in time were plotted for different shear rates and an explanation was advanced for the rheological behaviour found, based on the existing correlation between the structure and composition of the nutrient medium and the concentration and growth stage of the cellular mass.

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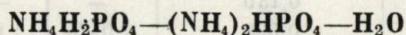
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STUDIUL COMPORTĂRII REOLOGICE A UNOR MEDII DE FERMENTAȚIE

(Rezumat)

A fost investigată comportarea reologică a unor medii de cultură de la obținerea penicilinei și streptomycinei. Rezultatele obținute au indicat, pentru ambele medii, o comportare tixotropă. Pentru partea ascendentă a curbelor s-a încercat o modelare de tip legea puterii. Datele experimentale au fost explicate prin existența unei corelații complexe între structura și compoziția mediului nutritiv și concentrația și stadiul de creștere a biomasei.

CARACTERIZAREA SOLUȚIILOR ÎN SISTEMUL TERNAR



DE

CAROLINA HAGIU și C. CALISTRU

1. Introducere

Amonizarea soluțiilor de acid fosforic — proces chimic principal în tehnologia îngrășămintelor complexe N—P sau N—P—K — conduce la obținerea, ca produse intermediare, a soluțiilor în sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4 - (\text{NH}_4)_2\text{HPO}_4 - \text{H}_2\text{O}$. Caracterizarea soluțiilor în acest sistem, în scopul utilizării datelor pentru controlul și conducerea științifică a procesului, implică cunoașterea proprietăților fizice, chimice, termodinamice și tehnologice. Dintre acestea, o mare importanță o prezintă proprietățile fizice generale (densitatea, viscozitatea, temperatura de fierbere) precum și proprietățile termodinamice.

Din analiza literaturii de specialitate referitoare la caracterizarea soluțiilor în sistemele N—P se constată, ca aspect general, existența unui număr restrâns de date experimentale care se referă la proprietățile fizice generale și de echilibru pentru sistemele pure $\text{NH}_4\text{H}_2\text{PO}_4 - \text{H}_2\text{O}$ [1]...[7] și $(\text{NH}_4)_2\text{HPO}_4 - \text{H}_2\text{O}$ [8]...[10]. Pentru sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4 - (\text{NH}_4)_2\text{HPO}_4 - \text{H}_2\text{O}$ sînt cunoscute numai proprietățile de echilibru lichid—solid și lichid—vapori [11]...[14].

Pentru a oferi unităților producătoare de îngrășămintă complexe datele necesare controlului și conducerii științifice a procesului de amonizare și pentru a completa fondul de date existent în literatură, în lucrarea de față se prezintă rezultatele experimentale referitoare la caracterizarea, prin proprietăți fizice generale, a soluțiilor în sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4 - (\text{NH}_4)_2\text{HPO}_4 - \text{H}_2\text{O}$.

2. Rezultate experimentale

S-au determinat densitatea, viscozitatea și temperatura de fierbere a soluțiilor în sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4 - (\text{NH}_4)_2\text{HPO}_4 - \text{H}_2\text{O}$, de compoziții corespunzătoare gradelor de amonizare variind între 1,3 și 1,7 [15] și la temperaturi de 25°, 35°, 50° și 75°C. Pentru obținerea soluțiilor de concentrații prestabilite s-au utilizat substanțe chimic pure, cu $\pm 0,1\%$ impurități. Tehnica de experimentare adoptată fiind cea clasică [16], [17] s-au asigurat și respectat condițiile de reproductibilitate a datelor experimentale.

Rezultatele experimentale sînt prezentate în tabelele 1...3.

Tabloul 1

Densitatea soluțiilor în sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4 - (\text{NH}_4)_2\text{HPO}_4 - \text{H}_2\text{O}$:
($\rho \cdot 10^{-3}$, $[\text{kg/m}^3]$)

Gradul de amonizare	Compoziția soluției		Temperatura, [°C]			
	$\bar{X}_{\text{NH}_4\text{H}_2\text{PO}_4}$	$\bar{X}_{(\text{NH}_4)_2\text{HPO}_4}$	25	35	50	75
1,3	0,05	0,024	1,0395	1,0360	1,0300	1,0175
	0,10	0,049	1,0800	1,0750	1,0700	1,0575
	0,15	0,073	1,1285	1,1275	1,1205	1,1074
	0,20	0,098	1,1665	1,1750	1,1600	1,1450
	0,30	0,130	—	—	—	1,2112
1,4	0,05	0,038	1,0475	1,0450	1,0395	1,0325
	0,10	0,076	1,1012	1,0925	1,0875	1,0750
	0,15	0,114	1,1482	1,1375	1,1325	1,1204
	0,20	0,153	1,2050	1,1925	1,1875	1,1726
	0,30	0,215	—	—	—	1,2600
1,5	0,05	0,057	1,0650	1,0550	1,0504	1,0426
	0,10	0,114	1,1255	1,1175	1,1104	1,0982
	0,15	0,172	1,1925	1,1775	1,1725	1,1576
	0,20	0,229	1,2550	1,2403	1,2351	1,2152
	0,30	0,333	—	—	—	1,3295
1,6	0,025	0,043	1,0403	1,0375	1,0306	1,0203
	0,050	0,086	1,0775	1,0708	1,0650	1,0578
	0,100	0,172	1,1595	1,1502	1,1475	1,1351
	0,150	0,258	1,2350	1,2302	1,2274	1,2152
	0,200	0,335	—	—	—	1,2925
1,7	0,025	0,067	1,0604	1,0575	1,0512	1,0413
	0,050	0,134	1,1075	1,1024	1,0950	1,0875
	0,075	0,201	1,1620	1,1580	1,1575	1,1418
	0,100	0,268	1,2204	1,2125	1,2075	1,1950
	0,150	0,295	—	—	—	1,3375

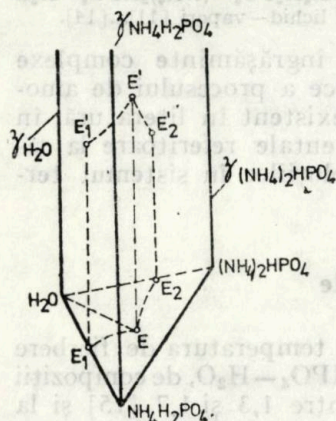


Fig.—1. Model spațial pentru reprezentarea dependenței proprietate — compoziție în sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4 - (\text{NH}_4)_2\text{HPO}_4 - \text{H}_2\text{O}$.

3. Prelucrarea datelor experimentale

Pentru reprezentarea grafică a dependenței proprietate—compoziție în sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4 - (\text{NH}_4)_2\text{HPO}_4 - \text{H}_2\text{O}$ s-a adoptat, ca model spațial, prisma cu baza un triunghi dreptunghic isoscel [18] a cărei schemă este prezentată în fig. 1.

Obținerea diagramelor plane s-a realizat prin proiecții ale modelului spațial și ale secțiunilor orizontale ale acestuia.

Reprezentarea grafică a dependenței densitate—compoziție pentru soluțiile din sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4 - (\text{NH}_4)_2\text{HPO}_4 - \text{H}_2\text{O}$ este redată în fig. 2 sub forma proiecțiilor modelului spațial pe diagrama compoziției și pe planul feței $\text{H}_2\text{O} - (\text{NH}_4)_2\text{HPO}_4$, la temperaturile de 25°, 50° și 75°C. Din această figură rezultă că pentru soluții de compoziții corespunzătoare

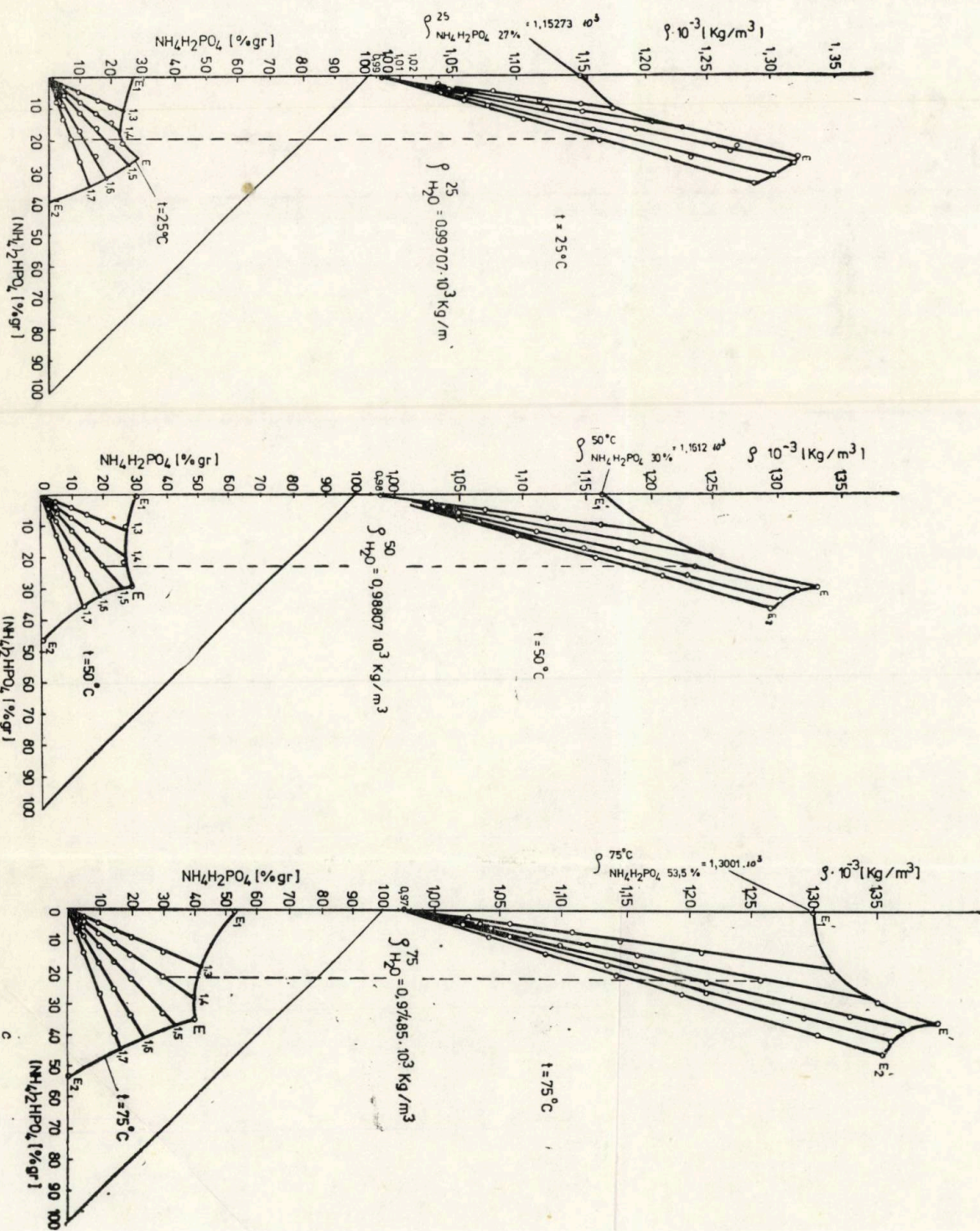


Fig. 2. — Reprezentarea dependenței densității — compoziție în sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4$ — $(\text{NH}_4)_2\text{HPO}_4$ — H_2O : a — $t = 25^\circ\text{C}$, b — $t = 50^\circ\text{C}$, c — $t = 75^\circ\text{C}$.

Tabelul 2.

Viscozitatea soluțiilor în sistemul ternar $NH_4H_2PO_4 - (NH_4)_2HPO_4 - H_2O$
($\nu \cdot 10^6$, $[m^2/s]$)

Gradul de amonizare	Compoziția soluției		Temperatura, [°C]			
	$\overline{X}_{NH_4H_2PO_4}$	$\overline{X}_{(NH_4)_2HPO_4}$	20	25	30	35
1,3	0,05	0,024	1,172	1,152	0,952	0,852
	0,10	0,049	1,465	1,305	1,171	1,061
	0,13	0,06	1,761	1,505	1,282	1,132
	0,15	0,073	2,302	1,763	1,502	1,328
	0,20	0,098	—	2,302	—	1,860
1,4	0,05	0,038	1,212	1,192	0,975	0,890
	0,10	0,076	1,603	1,412	1,286	1,152
	0,125	0,095	1,920	1,805	1,558	1,362
	0,15	0,114	2,405	2,223	1,902	1,703
	0,20	0,153	—	—	—	2,258
1,5	0,05	0,057	1,292	1,250	1,046	0,930
	0,075	0,086	1,461	1,342	1,162	1,082
	0,10	0,114	1,875	1,642	1,460	1,334
	0,13	0,150	2,322	2,223	1,960	1,701
	0,15	0,172	—	2,821	—	2,078
1,6	0,025	0,043	1,183	1,082	0,910	0,848
	0,05	0,086	1,402	1,341	1,110	1,005
	0,085	0,14	1,775	1,602	1,468	1,304
	0,10	0,172	2,295	2,023	1,842	1,549
	0,115	0,20	—	—	2,260	—
1,7	0,025	0,067	—	1,255	1,008	0,928
	0,05	0,134	—	1,505	1,328	1,220
	0,075	0,201	—	1,955	1,940	1,681
	0,10	0,268	—	3,605	3,085	2,712

Tabelul 3

Temperatura de fierbere a soluțiilor în sistemul ternar $NH_4H_2PO_4 - (NH_4)_2HPO_4 - H_2O$, [°C]

Gradul de amonizare	Compoziția soluției		Temperatura de fierbere, [°C]
	$\overline{X}_{NH_4H_2PO_4}$	$\overline{X}_{(NH_4)_2HPO_4}$	
1,3	0,05	0,024	101,72
	0,10	0,049	103,31
	0,15	0,073	105,10
	0,20	0,098	106,65
1,465	0,05	0,05	101,95
	0,10	0,10	104,05
	0,125	0,125	105,25
	0,15	0,15	106,45
1,57	0,05	0,076	102,15
	0,075	0,114	103,60
	0,10	0,15	105,10
	0,05	0,10	102,25
1,64	0,075	0,15	104,03
	0,10	0,20	106,18

dreptelor de amonizare, densitatea variază linear pînă la concentrația de saturație; această proprietate permite evaluarea densității soluțiilor de orice compoziție corespunzătoare unui grad de amonizare dat, precum și a densității soluțiilor saturate la temperatura respectivă.

Pentru a pune în evidență soluțiile din sistemul ternar cercetat, care au aceeași densitate, se efectuează secțiuni orizontale ale modelului spațial și se obțin diagramele reprezentate în fig. 3.

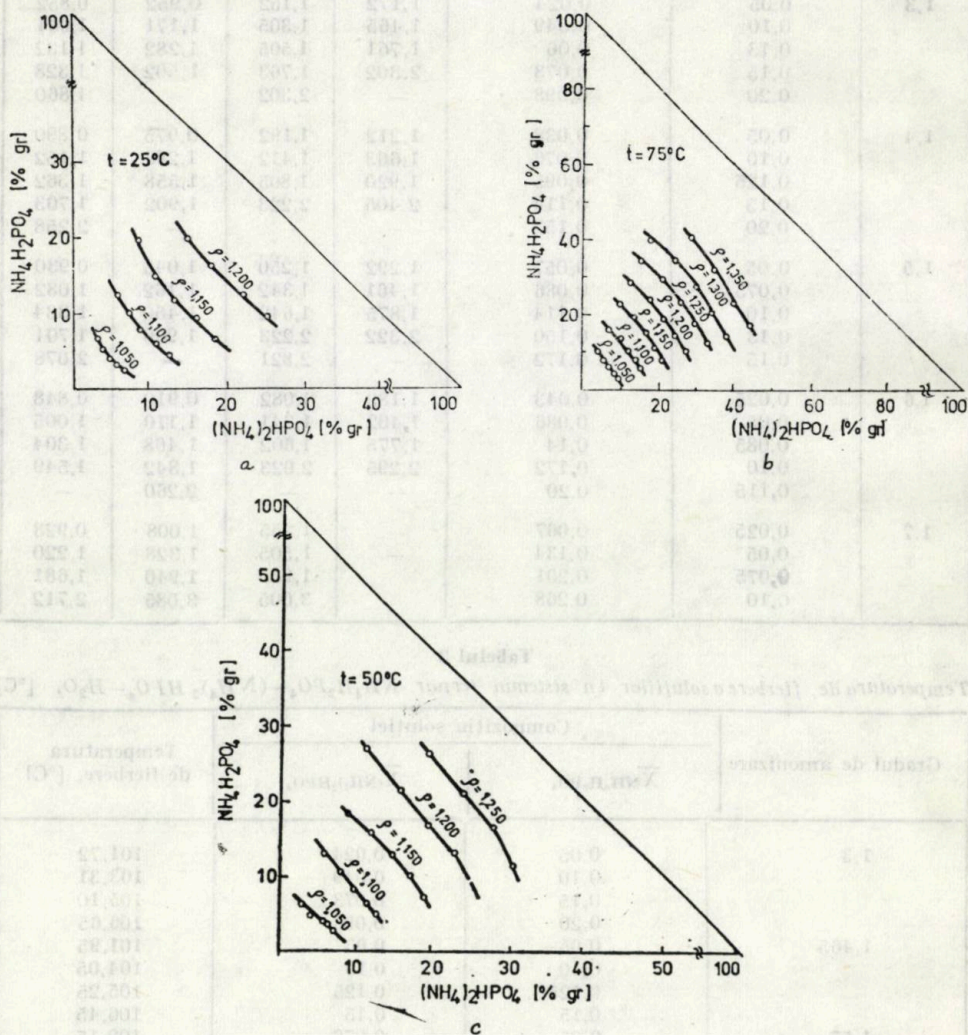
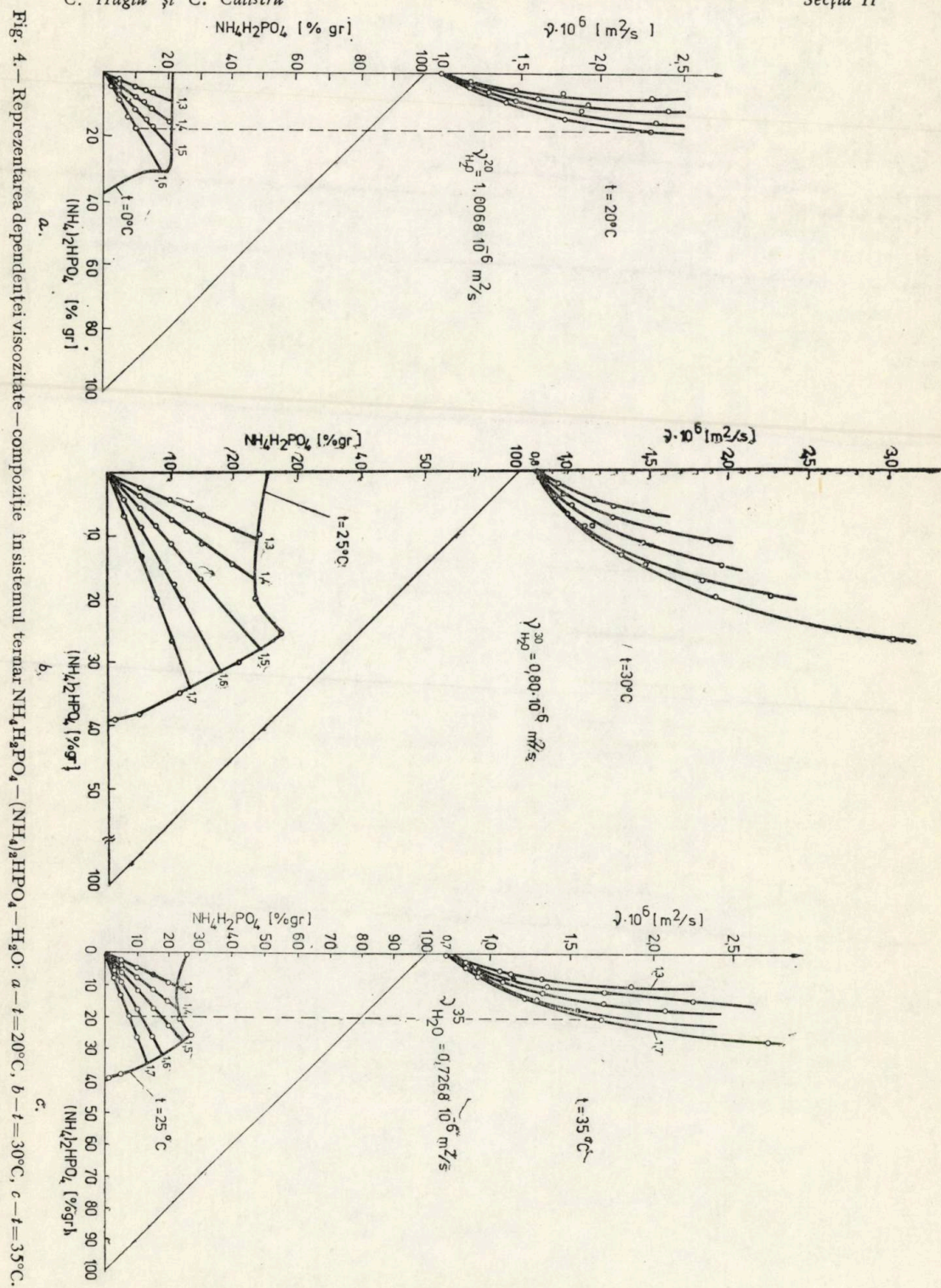


Fig. 3.—Proiecțiile secțiunilor orizontale ale densității: a— $t=25^\circ\text{C}$, b— $t=50^\circ\text{C}$, c— $t=75^\circ\text{C}$.

Reprezentarea grafică a dependenței viscozitate—compoziție în sistemul ternar studiat este dată în fig. 4, sub forma proiecțiilor pe diagrama compoziției și pe planul feței H_2O —(NH_4) $_2\text{HPO}_4$.

C. Hagiu și C. Calistru



Se constată că viscozitățile soluțiilor corespunzătoare unei drepte de amonizare se plasează pe o curbă. Pentru a pune în evidență soluțiile care au aceeași viscozitate, se efectuează secțiuni orizontale ale modelului spațial și se obțin rezultatele redată în fig. 5.

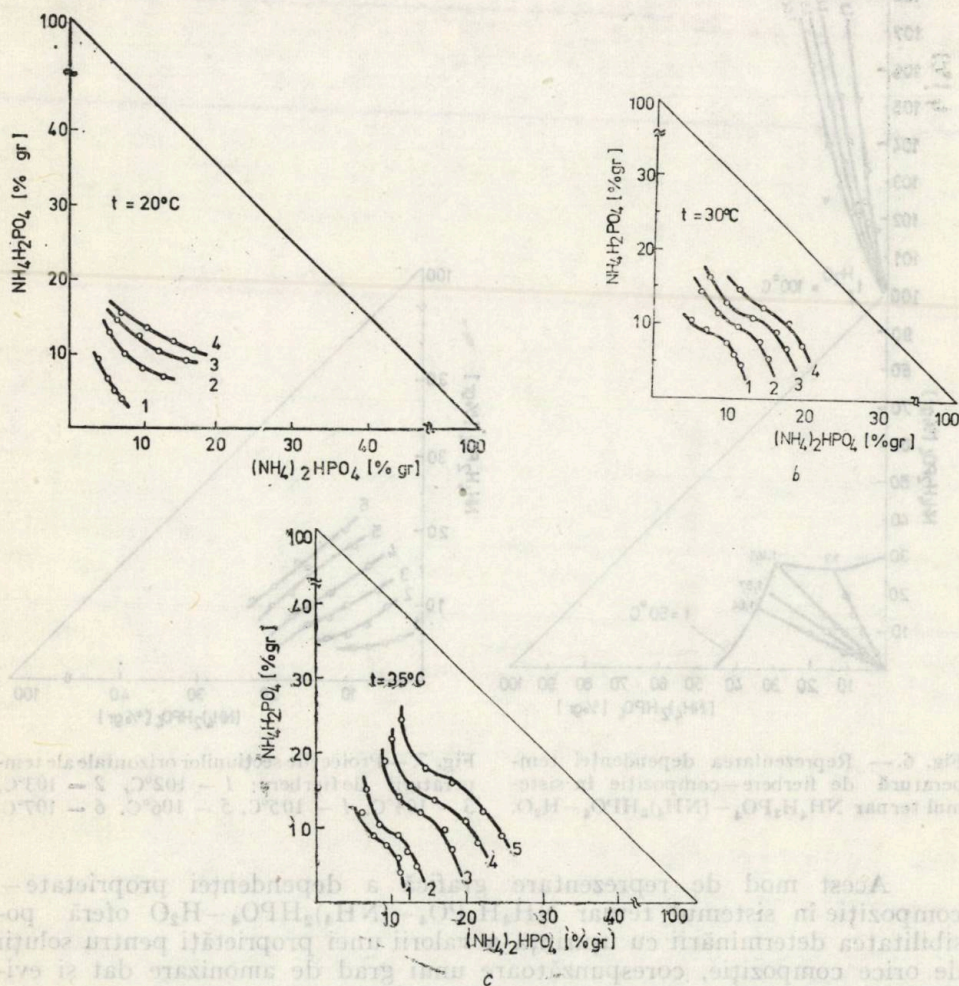


Fig. 5. — Proiecțiile secțiunilor orizontale ale viscozității :

a — $t = 20^{\circ}\text{C}$ (1 — $\nu = 1,3 \cdot 10^{-6} \text{ m}^2/\text{s}$, 2 — $\nu = 1,6 \cdot 10^{-6} \text{ m}^2/\text{s}$, 3 — $\nu = 1,9 \cdot 10^{-6} \text{ m}^2/\text{s}$, 4 — $\nu = 2,2 \cdot 10^{-6} \text{ m}^2/\text{s}$); b — $t = 30^{\circ}\text{C}$ (1 — $\nu = 1,2 \cdot 10^{-6} \text{ m}^2/\text{s}$, 2 — $\nu = 1,4 \cdot 10^{-6} \text{ m}^2/\text{s}$, 3 — $\nu = 1,6 \cdot 10^{-6} \text{ m}^2/\text{s}$, 4 — $\nu = 1,8 \cdot 10^{-6} \text{ m}^2/\text{s}$); c — $t = 35^{\circ}\text{C}$ (1 — $\nu = 1,1 \cdot 10^{-6} \text{ m}^2/\text{s}$, 2 — $\nu = 1,2 \cdot 10^{-6} \text{ m}^2/\text{s}$, 3 — $\nu = 1,5 \cdot 10^{-6} \text{ m}^2/\text{s}$, 4 — $\nu = 1,8 \cdot 10^{-6} \text{ m}^2/\text{s}$, 5 — $\nu = 2,2 \cdot 10^{-6} \text{ m}^2/\text{s}$).

Rezultatele experimentale referitoare la temperatura de fierbere în soluțiilor în sistemul $\text{NH}_4\text{H}_2\text{PO}_4 - (\text{NH}_4)_2\text{HPO}_4 - \text{H}_2\text{O}$ sînt reprezentate la

fig. 6, iar în fig. 7, prin proiecții ale modelului spațial, se pun în evidență soluțiile care au aceeași temperatură de fierbere.

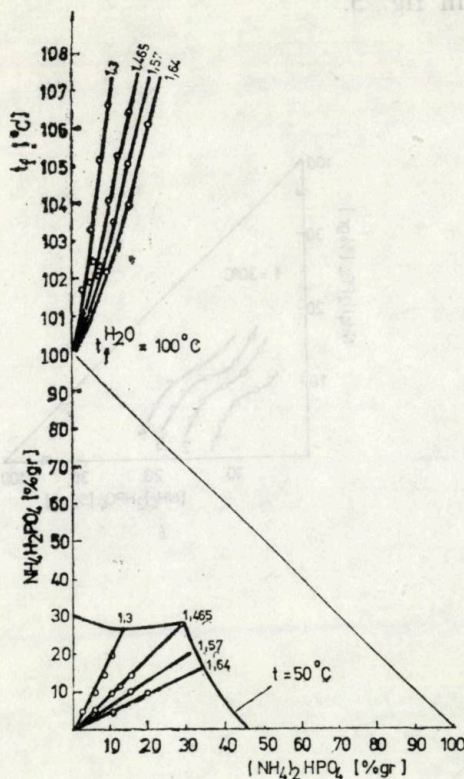


Fig. 6. — Reprezentarea dependenței temperatură de fierbere—compoziție în sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4$ — $(\text{NH}_4)_2\text{HPO}_4$ — H_2O .

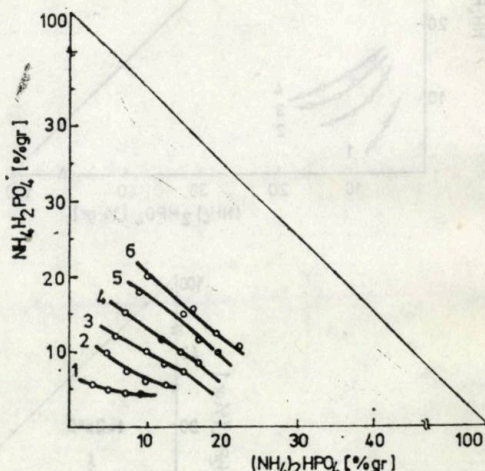


Fig. 7. — Proiecțiile secțiunilor orizontale ale temperaturii de fierbere; 1 — 102°C, 2 — 103°C, 3 — 104°C, 4 — 105°C, 5 — 106°C, 6 — 107°C.

Acest mod de reprezentare grafică a dependenței proprietate—compoziție în sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4$ — $(\text{NH}_4)_2\text{HPO}_4$ — H_2O oferă posibilitatea determinării cu ușurință a valorii unei proprietăți pentru soluții de orice compoziție, corespunzătoare unui grad de amonizare dat și evidențierii soluțiilor care au aceeași proprietate.

4. Concluzii

Cunoașterea proprietăților soluțiilor în sistemul ternar $\text{NH}_4\text{H}_2\text{PO}_4$ — $(\text{NH}_4)_2\text{HPO}_4$ — H_2O este absolut necesară pentru controlul și conducerea științifică a procesului de amonizare a soluțiilor de acid fosforic, proces chimic principal în industria îngrășămintelor complexe.

S-au determinat densitatea și viscozitatea soluțiilor în sistemul ternar menționat, de compoziții corespunzătoare gradelor de amonizare varind între 1,3 și 1,7 și la temperaturi de 25°, 35°, 50° și 75°C, precum și temperatura de fierbere a acestora.

S-au prelucrat grafic rezultatele obținute utilizând drept model spațial pentru reprezentarea dependenței proprietate—compoziție, prisma cu baza un triunghi dreptunghic isoscel.

Acest mod de prelucrare grafică oferă avantajul determinării proprietăților soluțiilor de orice compoziție corespunzătoare unui grad de amonizare constant și punerii în evidență a soluțiilor care au aceeași proprietate. De asemenea, dat fiind faptul că densitatea soluțiilor în sistemul ternar cercetat variază liniar cu compoziția, se pot determina cu ușurință densitățile soluțiilor saturate corespunzătoare gradelor de amonizare $\eta_A = 1,3 \dots 1,7$ și la temperaturi de 25°, 50° și 75°C, ceea ce constituie un avantaj evident, soluțiile saturate fiind mai greu de manipulat în cercetarea experimentală.

Notații

- t — temperatura, [°C],
 x — fracție de masă,
 ρ — densitatea, [kg/m³],
 ν — viscozitatea cinematică, [m²/s],
 η_A — grad de amonizare.

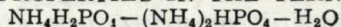
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SOLUTION PROPERTIES IN THE TERNARY SYSTEM



(Summary)

The experimental results regarding the general physical properties (density, viscosity and boiling temperature) of the solutions in ternary systems of compositions corresponding to ammonization degree of 1.3...1.7, at temperatures varying between 20° and 75°C are reported.

The graphical representations of the correlation property—composition using as spatial model the prism with basis an isosceles right angled triangle offer the advantages of determining quickly the property of a solution of any composition, for a given ammonisation degree, making evident the solutions with the same property, as well as determining the densities of saturated solutions at the experimental temperatures.

RECHERCHES CONCERNANT LE PROCÉDÉ DE SÉPARATION DU CUIVRE DES SOLUTIONS ACIDES DE CHLORURES PAR LA MÉTHODE DE LA CÉMENTATION AVEC LE FER

PAR

ȘT. IVĂȘCAN et FLORIN BANDRABUR

1. Introduction

Le procédé de séparation du cuivre, par cémentation, des solutions de sulfate de cuivre, est étudié en détail dans la littérature de spécialité [1]...[3].

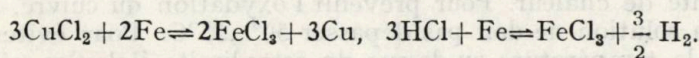
Par l'utilisation de certains métaux à potentiels plus électronégatifs que celui du cuivre (par exemple de fer) et des solutions de sulfate de cuivre en présence de l'acide sulfurique, il est possible d'obtenir des poudres de cuivre ou des dépôts d'oxydes de cuivre. Parallèlement avec l'obtention du „cément“ de cuivre, en fonction de la technologie utilisée, on peut obtenir aussi d'autres produits (FeSO_4 , CuSO_4) [4], [5].

Quant à la séparation du cuivre des solutions de chlorures on dispose seulement de quelques informations sommaires [6].

Dans ce travail on présente les résultats des recherches effectuées en vue de la séparation du cuivre des solutions de chlorure de cuivre et d'acide chlorhydrique libre, par la méthode de cémentation avec le fer.

2. Considérations théoriques

Les réactions chimiques du procédé de cémentation sont les suivantes:



Le procédé de cémentation est un processus du type adsorption—réaction—formation et croissance des germes [7]. Pour établir les équations algébriques du bilan des matériaux on doit définir tout d'abord les degrés de transformation:

$$\eta_{\text{CuCl}_2} = \frac{\eta_{\text{CuCl}_2}^0 - \eta_{\text{CuCl}_2}}{\eta_{\text{CuCl}_2}^0} = \frac{\eta_{\text{Fe}}^0 - \eta_{\text{Fe}}}{\frac{2}{3}\eta_{\text{CuCl}_2}^0} = \frac{\eta_{\text{FeCl}_3}}{\frac{2}{3}\eta_{\text{CuCl}_2}} = \frac{\eta_{\text{Cu}}}{\eta_{\text{CuCl}_2}^0},$$

$$\eta_{\text{HCl}} = \frac{\eta_{\text{HCl}}^0 - \eta_{\text{HCl}}}{\eta_{\text{HCl}}^0} = \frac{\eta_{\text{Fe}}^0 - \eta_{\text{Fe}}}{\frac{1}{3} \eta_{\text{HCl}}^0} = \frac{\eta_{\text{H}_2}}{\frac{1}{2} \eta_{\text{HCl}}^0}.$$

Les équations du bilan des matériaux par composants (nombre de moles) sont présentées dans le tableau 1.

Tableau 1
Équations algébriques du bilan de matériaux (moles)

Composant	Phase	Matières entrées	Matières sorties
CuCl ₂	Liquide	$n_{\text{CuCl}_2}^0$	$n_{\text{CuCl}_2} = n_{\text{CuCl}_2}^0 (1 - \eta_{\text{Cu}^{2+}})$
FeCl ₃	Liquide	—	$n_{\text{FeCl}_3} = \frac{2}{3} n_{\text{CuCl}_2}^0 \eta_{\text{Cu}^{2+}} + \frac{1}{3} n_{\text{HCl}}^0 \eta_{\text{HCl}}$
HCl	Liquide	n_{HCl}^0	$n_{\text{HCl}} = n_{\text{HCl}}^0 (1 - \eta_{\text{HCl}})$
H ₂ O	Liquide	$n_{\text{H}_2\text{O}}^0$	$n_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}}^0$
Fe	Solide	n_{Fe}^0	$n_{\text{Fe}} = n_{\text{Fe}}^0 - \frac{2}{3} n_{\text{CuCl}_2}^0 \eta_{\text{Cu}^{2+}} - \frac{1}{3} n_{\text{HCl}}^0 \eta_{\text{HCl}}$
Cu	Solide	—	$n_{\text{Cu}} = n_{\text{CuCl}_2}^0 \eta_{\text{Cu}^{2+}}$
H ₂	Gaz	—	$n_{\text{H}_2} = \frac{1}{2} n_{\text{HCl}}^0 \eta_{\text{HCl}}$
Impuretés	Liquide Solide	$n_{\text{A}''}^0$	$n_{\text{A}''} = n_{\text{A}''}^0$

3. Partie expérimentale

On a étudié par voie expérimentale les possibilités de séparation du cuivre contenu dans les solutions résiduelles de chlorure de cuivre (80...120 g/l Cu²⁺ et 180...200 g/l HCl libre) par cémentation avec des barres et plaques de fer.

Le dépôt de cuivre obtenu a un aspect spongieux, et lorsqu'il atteint une grosseur moyenne de 2,5...4 mm se décolle de la surface du fer et se dépose au fond du réacteur.

Sur la surface du fer reste une couche noire d'une grosseur de 0,5...1 mm, qui se sépare avec difficulté. La séparation du cuivre de la solution se réalise facilement par décantation. Pendant la cémentation se dégage une grande quantité de chaleur. Pour prévenir l'oxydation du cuivre, la température de la solution ne doit pas dépasser 50°...55°C. Pour éviter l'augmentation de la température au-dessus de cette limite ils'avère nécessaire la dilution de la solution initiale jusqu'à 18...25 g/l Cu²⁺.

Les courbes cinétiques de la variation de la quantité de cuivre déposée sur le fer en fonction de temps, utilisant des solutions de chlorure de cuivre (CuCl₂) avec un contenu de 18,176 g/l Cu²⁺ sur les surfaces de réactions de 34, 68 et 102 cm², sont représentées dans les Fig. 1...3.

L'analyse des résultats obtenus ont permis à établir que la dimension de la surface de réaction est un paramètre important qui assure la séparation totale du cuivre (Fig. 4).

Toute fois les données obtenues montrent que l'augmentation des surfaces de réaction et la dilution de la solution au dessus de certaines valeurs ne sont pas justifiées, car en ce qui concerne le temps de séparation des ions Cu^{2+} , il ne se réduit pas. En même temps l'augmentation des surfaces de réaction peut déterminer le chauffage de la solution dans les premières minutes, favorisant le processus de l'oxydation du cuivre.

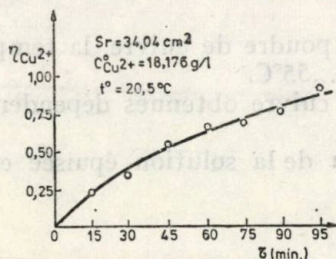


Fig. 1. — Courbe cinétique $\eta_{\text{Cu}^{2+}}(\tau)$ pour la surface de 34 cm^2 .

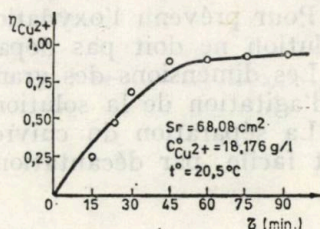


Fig. 2. — Courbe cinétique $\eta_{\text{Cu}^{2+}}(\tau)$ pour la surface de 68 cm^2 .

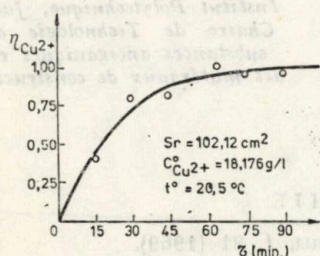


Fig. 3. — Courbe cinétique $\eta_{\text{Cu}^{2+}}(\tau)$ pour la surface de 102 cm^2 .

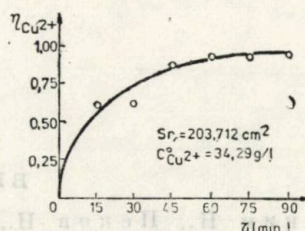


Fig. 4. — Courbe cinétique $\eta_{\text{Cu}^{2+}}(\tau)$ pour la surface de 204 cm^2 .

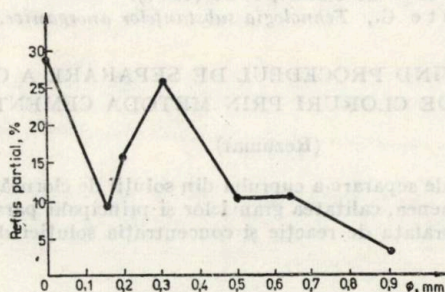


Fig. 5. — Les résultats de l'analyse granulométrique du dépôt de cuivre obtenu.

Dans la Fig. 5 est représentée la courbe granulométrique de la poudre de cuivre obtenue. Afin que les granules aient des dimensions déterminées il est nécessaire à agiter le milieu de réaction.

4. Conclusions

1. On a étudié le procédé de séparation du cuivre des solutions de chlorure cuivrique, avec un contenu variable de HCl libre, par cémentation avec le fer.

2. Les paramètres qui peuvent influencer la vitesse de la cémentation sont la concentration de la solution en ions de cuivre et la surface de réaction.

3. Pour prévenir l'oxydation de la poudre de cuivre, la température de la solution ne doit pas dépasser 50°...55°C.

4. Les dimensions des granules de cuivre obtenues dépendent de la vitesse d'agitation de la solution.

5. La séparation du cuivre obtenu de la solution épuisée est relativement facile, par décantation.

Notations

n^0 — nombre de moles de la masse de réaction initiale,

n — nombre de moles de la masse de réaction finale,

$\emptyset$ — diamètre de l'oeil du sas, [mm].

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Institut Polytechnique, Jassy,
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CERCETĂRI PRIVIND PROCEDEUL DE SEPARARE A CUPRULUI DIN SOLUȚII ACIDE DE CLORURI PRIN METODA CEMENTĂRII CU FER

(Rezumat)

S-a studiat procesul de separare a cuprului din soluții de clorură cuprică prin cementare cu fer. S-a studiat, de asemenea, calitatea granulelor și principalii parametri care influențează procesul: temperatura, suprafața de reacție și concentrația soluției de ioni Cu^{2+} .

SYNTHESIS OF ANTICANCEROUS SUBSTANCES

SYNTHESIS AND STUDY OF THE TOXICITY OF CERTAIN DI-(β -CHLOROETHYL)-AMIDES CONTAINING *p*-(NITROCYNAMOYL)- α -AMINOACIDS SUPPORT

BY

C. H. BUDEANU, ELENA IVAS and VALERIU ȘUNEL

1. Introduction

At present the research try to improve the biological characteristics of the alkylating agents, mainly to increase the therapeutic index while the hematopoietic toxicity decreases. It is known that the toxicity of N-mustards grows as the nonparticipating electrons of nitrogen atom are more available. Nonparticipating electrons of nitrogen atom were blocked by different methods, one of which is their implication into an amidic conjugation system [1]...[6]. The products having such a structure proved themselves to be more stable towards water and other nucleophilic reagents.

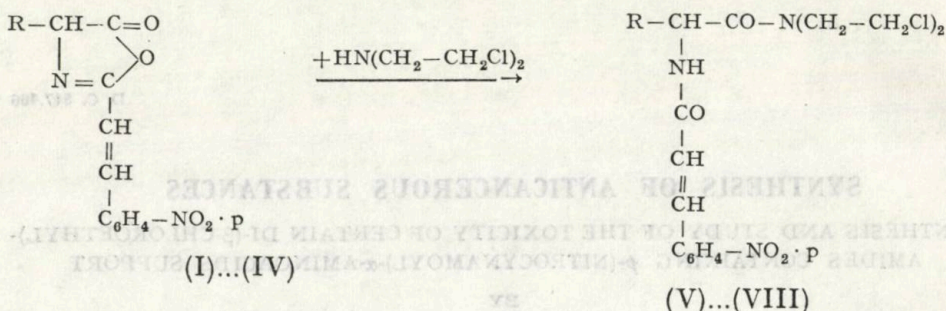
Also, it is supposed that the initial amidic structures of these compounds are the inactive forms of „the transport“ of the drug which *in vivo* after the penetration in the tumour cells transform into active forms of di-(β -chloroethyl)-amine, owing to certain reactions which can take place at this level. Starting from these results we have synthesised new types of alkylating agents in which the availability of chlorine atoms should be much decreased.

2. Results and Discussions

The fact that Δ^2 -oxazolinones-5, which we have synthesised previously [7], showed a great affinity towards certain nucleophilic reactants encouraged us to perform their reaction with di-(β -chloroethyl)-amine to obtain di-(β -chloroethyl)-amides of the corresponding *p*-(nitrocynamoyl)- α -aminoacids. This idea was suggested to us also by the fact that Δ^2 -oxazolinones-5 react in a similar manner with monoethanol amine [2].

The first compounds studied from the point of view of their reaction with di-(β -chloroethyl)-amine are Δ^2 -oxazolinones-5, (I)...(IV). The reaction was carried out by mixing the components (molar ratio Δ^2 -oxazolinone: di-(β -chloroethyl)-amine is 1 : 2) in anhydrous dioxane and heating the mixture for 90 min. at 50°...60°C. In these way we prepared di-(β -chloroethyl)- α -amides derived from *p*-nitrocynamoyl-DL-asparagic acid, *p*-nitrocynamoyl-DL-asparagine, *p*-nitrocynamoyl-DL-glutamic acid and *p*-nit-

rocynamoyl-DL-methionine (V)...(VIII). The products (V)...(VIII) are cristaline, have sharp melting points and the yelds are 40...53%.



(I), (V) R = $-\text{CH}_2-\text{COOH}$; (II), (VI) R = $-\text{CH}_2-\text{CO}-\text{NH}_2$; (III), (VII) R = $-(\text{CH}_2)_2-\text{COOH}$
 (IV), (VIII) R = $-(\text{CH}_2)_2-\text{S}-\text{CH}_3$

Their structure was confirmed by elemental analysis and IR spectra. All products showed absorption peaks at $1640...1675\text{ cm}^{-1}$ and $1520...1535\text{ cm}^{-1}$, characteristic for amide groups and at $725...770\text{ cm}^{-1}$ for C-Cl band from di-(β -chloroethyl)-amine [8].

As these new four products which we have synthetised may have antitumour activity as antimetabolitics or alkylating agents, we tested their toxicity and we found the *per os* maximum tolerable dose (DL_0), the minimum lethal dose (DL_{100}) and DL_{50} . To determine the acute toxicity, we used the indications by Buchel [9] who showed that the most sensitive animals are the mice, and their selection and care were done using Covaletsch's indications [10]. The weight of the animals was $20 \pm 2\text{ g}$ and the batches were composed each of 10 animals of both sexes, with a safety limit of 90%. Water insoluble products were brought to suspension by grinding them in physiological serum and they were daily administered with an esophagus sound. After the administration of the product, the animals were watched every 6 hours, noticing all the modifications. The lethality was counted after 48 hours from the oral administration. So we determined DL_{50} *per os* using the method [11] with three successive doses with 1.2 ratio orally. The obtained results are given in Table 1. As

Table 1

Toxicity of the Tested Compounds

Compound	Test animals	Administration	DL_{50} mg/Kilobody
(V)	mice	p.o.	300
(VI)	mice	p.o.	280
(VII)	mice	p.o.	180
(VIII)	mice	p.o.	220

it can be seen from these table, by grafting di-(β -chloroethyl)-amino group on the nucleus of *p*-nitrocynamoyl- α -aminoacids, we obtained products of a lower toxicity compared to N-mustard. We consider that this result is normal, taking into account some literature data according to which the utilization of N-acyl-aminoacids as transport reagents for the cytostatic group has a positive influence on the decrease of its toxicity [12]...[15].

3. Experimental

a) α -[Di-(β -chloroethyl)-amide] of *N*-(*p*-nitrocynamoyl)-DL-asparagic acid (V)

In a round bottom flask fitted with condenser 0.01 moles 2- β -(*p*-nitrostyryl)-4-(β -carboxymethyl)- Δ^2 -oxazolinone-5 (I), 30 ml anhydrous dioxane and 0.02 moles di-(β -chloroethyl)-amine were introduced. The reaction mixture was heated at 50°...60°C for one hour. Dioxane was distilled of under reduced pressure, at 40°...45°C. The viscous product which remained in the flask was washed thoroughly with anhydrous ether until it turned into a fine precipitate and dispersed into ether. It was filtered and dried in a vacuum oven at 40°...45°C for 10 hours. A white solid product with melting point at 174°...176°C and the yield 52.8% was obtained.

Analysis: $C_{17}H_{19}Cl_2N_3O_8$	C%	H%	N%	Cl%
Calculated:	47.23	4.43	9.72	16.40
Found:	46.78	4.52	9.58	16.78
	46.75	4.68	9.60	16.88

The IR Spectrum (KBr): 3 200 cm^{-1} , 3 280 cm^{-1} ν_{N-H} amide; 1 640 cm^{-1} $\nu_{C=O}$ amide; 1 532 cm^{-1} amide II band; 1 455 cm^{-1} $\nu_{C=O}$; 1 340 cm^{-1} , 1 580 cm^{-1} ν_{NO_2} symmetric and asymmetric; 840 cm^{-1} disubstituted benzene ring; 725 cm^{-1} ν_{C-Cl} .

b) α -[Di-(β -chloroethyl)-diamide] of *N*-(*p*-nitrocynamoyl)-DL-asparagic acid (VI)

This compound was synthesised in a similar manner as the compound (V), resing 0.01 moles 2- β -(*p*-nitrostyryl)-4-(β -amidomethyl)- Δ^2 -oxazolinone-5 (II), 50 ml anhydrous dioxane and 0.02 moles di-(β -chloroethyl)-amine. The reaction product is a white powder and it melts at 103°...104°C; yield 50.5%.

Analysis: $C_{17}H_{20}Cl_2N_4O_5$	C%	H%	N%	Cl%
Calculated:	47.34	4.67	12.99	16.44
Found:	46.83	5.02	13.43	16.88
	46.85	5.00	13.28	16.68

The IR Spectrum (KBr): 3 248 cm^{-1} ν_{N-H} ; 1 620 cm^{-1} , 1 660 cm^{-1} $\nu_{C=O}$ amide; 1 520 cm^{-1} amide II band; 1 465 cm^{-1} $\nu_{C=C}$; 1 340 cm^{-1} , 1 560 cm^{-1} ν_{NO_2} symmetric and asymmetric; 840 cm^{-1} disubstituted benzene; 725 cm^{-1} ν_{C-Cl} .

c) α -[Di-(β -chloroethyl)-amide] of *N*-(*p*-nitrocynamoyl)-DL-glutamic acid (VII)

This compound was synthesised similarly to the compound (V), resing 0.1 moles 2- β -(*p*-nitrostyryl)-4-(β -carboxyethyl)- Δ^2 -oxazolinone-5 (III), 35 ml anhydrous dioxane and 0.02 moles di-(β -chloroethyl)-amine. The reaction product is a light-yellow powder and it melts at 94°...96°C. Yield 39.7%.

Analysis: $C_{18}H_{21}Cl_2N_3O_8$	C%	H%	N%	Cl%
Calculated:	48.44	4.74	9.41	15.88
Found:	49.00	4.29	9.64	15.42
	48.80	4.30	9.80	16.00

The IR Spectrum (KBr): 3 350 cm^{-1} ν_{N-H} ; 1 640 cm^{-1} , 1 675 cm^{-1} $\nu_{C=O}$ amide; 1 520 cm^{-1} amide II band; 1 470 cm^{-1} $\nu_{C=C}$; 1 340 cm^{-1} , 1 558 cm^{-1} ν_{NO_2} symmetric and asymmetric; 880 cm^{-1} disubstituted benzene ring; 770 cm^{-1} ν_{C-Cl} .

d) α -[di-(β -chloroethyl)-amide] of *N*-(*p*-nitrocynamoyl)-DL-methionin (VIII)

This compound was synthesised similarly to the compound (V) using 0.005 moles 2- β -(*p*-nitrostyryl)-4-(β -methylthioethyl)- Δ^2 -oxazolinone-5 (IV), 50 ml anhydrous dioxane and 0.01 moles di-(β -chloroethyl)-amine. The reaction product is a white powder and it melts at 177°...179°C. Yield 42.1%.

<i>Analysis</i> : $C_{18}H_{23}Cl_2N_3O_4S$	C %	H %	N %	Cl %
Calculated :	48.21	5.17	9.39	15.81
Found :	48.52	5.37	9.49	16.05
	48.70	5.57	9.55	16.20

The IR Spectrum (KBr) : 3 330 cm^{-1} $\nu_{\text{N-H}}$ amide; 1 640 cm^{-1} , 1 660 cm^{-1} $\nu_{\text{C=O}}$ amide 1 535 cm^{-1} amide II band; 1 485 cm^{-1} $\nu_{\text{C=C}}$; 655 cm^{-1} $\nu_{\text{C-S}}$; 1 340 cm^{-1} , 1 560 cm^{-1} ν_{NO_2} symmetric and asymmetric; 860 cm^{-1} disubstituted benzene ring; 728 cm^{-1} $\nu_{\text{C-Cl}}$.

4. Conclusions

Four new N-mustards (V)...(VIII) with N-(*p*-nitrocynamoyl)- α -aminoacids support have been synthesised by the decyclization of certain β -(*p*-nitrostyryl)- Δ^2 -oxazolinone-5 (I)...(IV).

The structure of the resulted compounds was confirmed by elemental analysis and IR spectra.

The toxicity of the new N-mustards (V)...(VIII) has been studied and DL_{50} was determined. Their low toxicity, comparable to that of the free cytostatic group, recommends these compounds to be used in the experimental treatment of certain malignant tumour.

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SINTEZE DE SUBSTANȚE ANTICANCEROASE

Sinteza și studiul toxicității unor di-(β -cloretile)-amide cu suport de *p*-(nitrocinaoil)- α -aminoacizi
(Rezumat)

În scopul obținerii de noi substanțe alchilante cu toxicitate scăzută s-au sintetizat azotiperite cu suport de *p*-(nitrocinaoil)- α -aminoacizi prin deciclizarea unor 2- β -(*p*-nitrostiril)- Δ^2 -oxazolinone-5 sub acțiunea di-(β -cloretile)-aminei. S-a studiat toxicitatea lor stabilindu-se DL_{50} .

ACȚIUNEA DIENOFILELOR ACETILENICE ȘI A UNOR HETEROCUMULENE ASUPRA SĂRURILOR DE N-FENACIL- ȘI N-CARBETOXIMETIL-BENZTIAZOLULUI

DE

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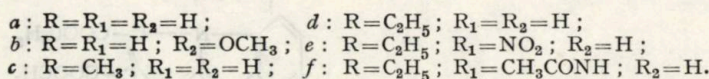
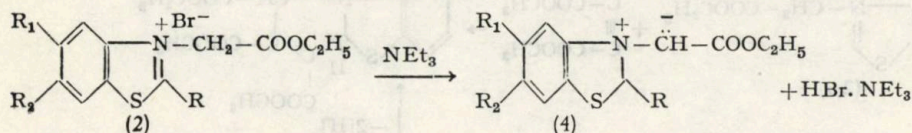
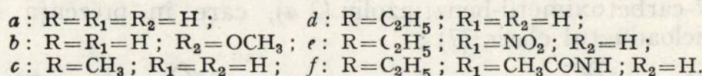
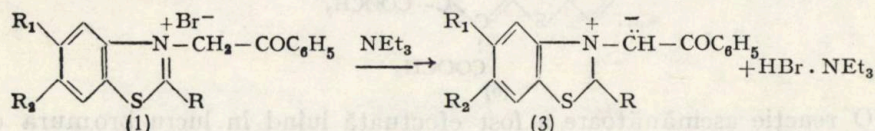
1. Introducere

În cercetările noastre ne-am propus să efectuăm reacții de cicloadiție a benziazoliu-ilidelor formate *in situ* la acetilene și compuși cu legături C=N activate în scopul: a) lărgirii gamei reacțiilor de cicloadiție 3+2 dipolară în clasa benziazolului; b) obținerii de noi structuri heterociclice derivate de la benziazol, inaccesibile sau greu de obținut pe alte căi.

2. Rezultate și discuții

După apariția lucrărilor lui R. Huisgen [1] reacțiile de cicloadiție 3+2 dipolară au atras atenția chimiștilor organicieni. Cicloadițiile dipolare 1,3 la alchene și acetilene activate reprezintă o cale importantă de acces la heterocicli cu cinci atomi. Acest fapt explică de altfel interesul de care se bucură în continuare astfel de reacții.

Sărurile de N-fenacil- și N-carbetoximetil-benziazoliu [2], la tratare cu trietilamină, ar trebui să treacă în ilidele corespunzătoare [3], [4]:



Benziazoliu-ilidele, spre deosebire de alte benzoil-metilide și carbaloxi-metilide [3]...[7] nu sînt stabile și deci nu au putut fi izolate. Din

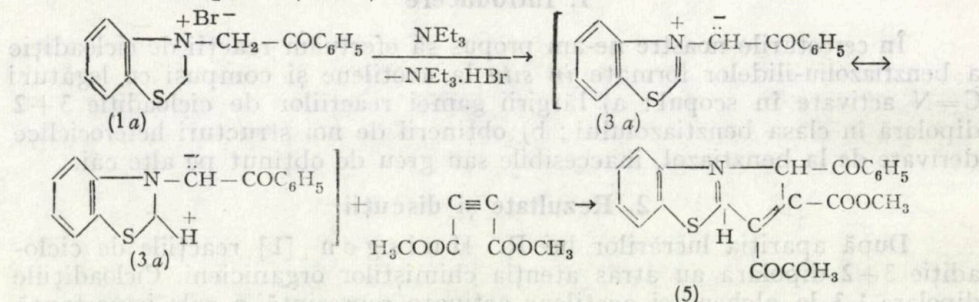
aceste motive am încercat introducerea în sistem (sare de benziazoliu și trietilamină) a unui reactant dienofil care să reacționeze cu ilida formată *in situ*, folosind condiții de reacție destul de blânde pentru a împiedica deschiderea ciclului.

Benziazoliu-ilidele admit o structură 1,3-dipolară care le conferă capacitatea de a lua parte direct la reacții de cicloadiție cu diferiți agenți dipolarofili. Aceste reacții constituie un argument în favoarea apariției unor intermediari cu structură ilidică.

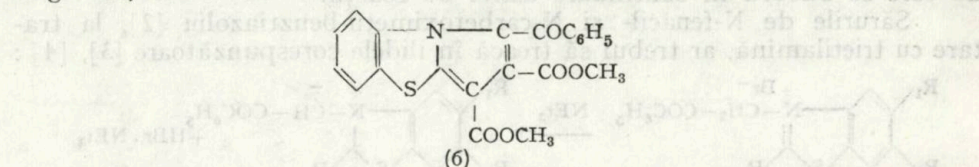
Este cunoscut de mult timp că acetilenele activate cu grupări cu efect $-I$ și $-E$ sînt utilizate ca filodiene în reacțiile de cicloadiție dipolară a ilidelor [8]...[10].

În cercetările noastre am studiat reacția acetilendicarboxilatului de metil DMAD cu benziazoliu-benzoil-metilida (3a) și benziazoliu-carbetoxi-metilida (4a). Ilidele respective au fost obținute *in situ* la tratarea bromurilor corespunzătoare cu trietilamină în mediu de clorură de metilen.

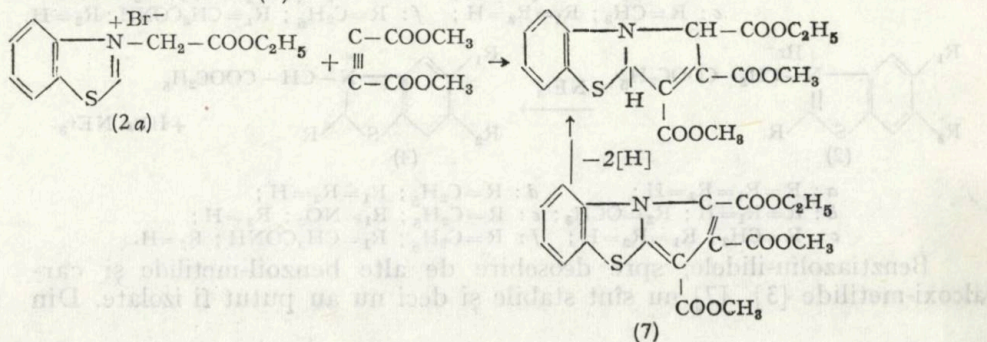
Reacția ilidei (3a) cu DMAD a condus la închiderea unui nou ciclu de 5 atomi de pirolo-/2,1-b/-benziazol:



Produsul (5), prin fierbere în acetonitril, suferă un proces de dehidrogenare, conducînd la:



O reacție asemănătoare a fost efectuată luînd în lucru bromura de N-carbetoximetil-benziazoliu (2a), care în prezența DMAD conduce la cicloaductul clasic (7):

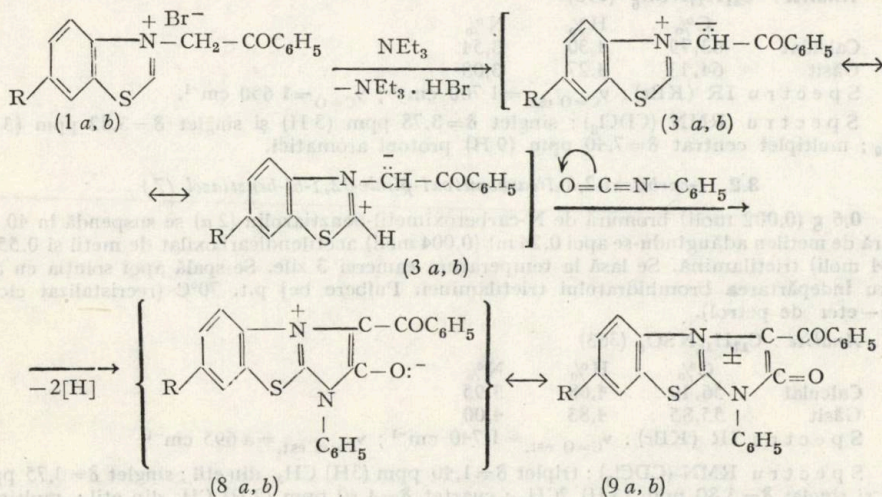


Trebuie să se admită că în prima etapă se formează produsul hidrogenat care se dehidrogenează sub influența oxigenului din aer sau a unei părți din DMAD. Forța motoare a acestei dehidrogenări trebuie căutată în refacerea aromaticității în produsul final de reacție.

Alte filodiene, și anume cele cu legături duble heteroatomice, pot da de asemenea cicloadiții la benziazoliu-ilide.

Pentru început am ales dintre aceste filodiene izocianatul de fenil, care formează cu ilidele carbon-azot două tipuri de produși de reacție. Cu ilide de structuri N-heteroatomice reactive s-au izolat produși de cicloadiție a izocianatului de fenil [11], [4], iar în alte cazuri intermediarul amfionic, obținut în prima treaptă a reacției de adiție, poate fi izolat sub forma unui produs stabil ca urmare a migrării unui proton [12], [13].

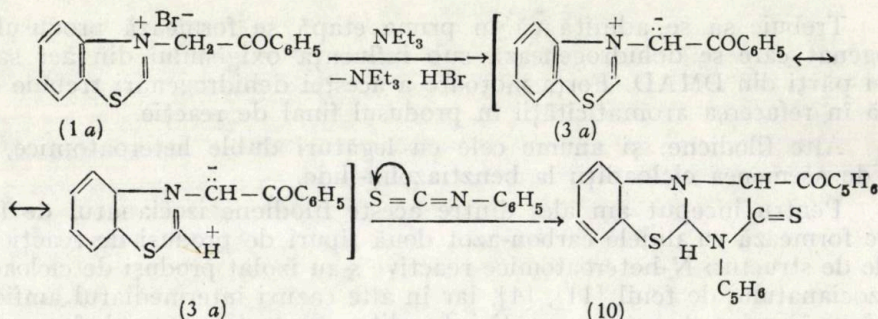
În cazul cercetat de noi izocianatul de fenil reacționează cu benziazoliu-benzoil-metilida (3 a) și cu 6-metoxi-benziazoliu-benzoil-metilida (3 b) formate *in situ* cu închiderea unui ciclu de 5 atomi după un mecanism concertat. S-a obținut astfel un produs de ciclizare, de structură mezoionică, (9), asemănător cu cei obținuți de S. S o t o și M. O h t a [13] în reacția izochinolinu-N-fenacilidei cu izocianat și izotiocianat de fenil.



Structura dipolară a benziazoliu-benzoil-metilidei (3 a), obținută din sarea corespunzătoare (1 a) *in situ*, este confirmată și prin reacția de cicloadiție cu izotiocianatul de fenil. Ca și izocianatul de fenil, izotiocianatul de fenil se comportă în reacțiile cu ilide ca o filodienă cu legătură dublă $\text{C}=\text{N}$. Izotiocianatul de fenil dă reacții de cicloadiție cu izochinolinu-N-fenacilida [12], pe când în cazul izochinolinu-carbetoxy-metilidei se obțin compuși ilidici disubstituiți la carbanion [14].

În încercările făcute cu izotiocianatul de fenil numai în cazul benziazoliu-benzoil-metilidei (3 a) s-a obținut un produs bine definit. Trebuie menționat că acest proces de ciclizare nu este însoțit de dehidrogenare.

Reacția decurge conform următorului mecanism :



3. Partea experimentală

3.1. 1-benzoil-2,3-dicarbometoxi-pirololo-[2,1-b]-benztiazol (6)

Se suspendă 0,34 g (0,001 moli) bromură de N-fenacil-benzotiazoliu (1 a) în 30 ml clorură de metilen și se adaugă apoi 0,13 ml (0,001 moli) acetilendicarboxilat de metil și 0,14 ml (0,001 moli) trietilamină. Se refluxează amestecul 5 min. și se lasă apoi la temperatura camerei 3 zile. Se îndepărtează bromhidratul trietilaminei prin spălare cu apă. Pulbere galbenă p.t. 90°C (recristalizat benzen-eter de petrol).

Analize: $C_{21}H_{17}NSO_5$ (395)

	C%	H%	N%
Calculat	63,79	4,30	3,54
Găsit	64,13	4,27	3,08

Spectru IR (KBr): $\nu_{C=O \text{ est.}} = 1760 \text{ cm}^{-1}$; $\nu_{C=O} = 1690 \text{ cm}^{-1}$.

Spectru RMN ($CDCl_3$): singlet $\delta = 3,78 \text{ ppm}$ (3 H) și singlet $\delta = 3,82 \text{ ppm}$ (3 H) $2CH_3$; multiplet centrat $\delta = 7,40 \text{ ppm}$ (9 H) protoni aromatici.

3.2. 1-carbetoxi-2,3-dicarbometoxi-pirololo-[2,1-b]-benztiazol (7)

0,6 g (0,002 moli) bromură de N-carbetoximetil-benzotiazoliu (2 a) se suspendă în 40 ml clorură de metilen adăugându-se apoi 0,24 ml (0,004 moli) acetilendicarboxilat de metil și 0,55 ml (0,004 moli) trietilamină. Se lasă la temperatura camerei 3 zile. Se spală apoi soluția cu apă pentru îndepărtarea bromhidratului trietilaminei. Pulbere bej p.t. 70°C (recristalizat cloroform-eter de petrol).

Analize: $C_{17}H_{15}NSO_6$ (363)

	C%	H%	N%
Calculat	56,19	4,68	3,95
Găsit	55,85	4,83	4,00

Spectru IR (KBr): $\nu_{C=O \text{ est.}} = 1740 \text{ cm}^{-1}$; $\nu_{C=O \text{ est.}} = 695 \text{ cm}^{-1}$.

Spectru RMN ($CDCl_3$): triplet $\delta = 1,40 \text{ ppm}$ (3H) CH_3 din etil; singlet $\delta = 3,75 \text{ ppm}$ (3 H) și singlet $\delta = 3,80 \text{ ppm}$ (3 H) $2CH_3$; cuartet $\delta = 4,40 \text{ ppm}$ (2 H) CH_2 din etil; multiplet centrat $\delta = 7,40 \text{ ppm}$ (4 H) protoni aromatici.

3.3. Anhidro-3-benzoil-2-hidroxi-imidazolo-[2,1-b]-benztiazolium-hidroxid (9 a).

0,34 g (0,001 moli) bromură de N-fenacil-benzotiazoliu (1 a) se suspendă în 30 ml clorură de metilen adăugându-se apoi 0,1 ml (0,001 moli) izocianat de fenil și 0,14 ml (0,0015 moli) trietilamină. Se refluxează amestecul 5 min. după care se lasă la temperatura camerei 3 zile, se spală cu apă distilată pentru îndepărtarea bromhidratului trietilaminei. Pulbere galbenă p.t. 110°C (recristalizat n. heptan).

Analize: $C_{22}H_{14}N_2SO_2$ (372)

	C%	H%	N%
Calculat	70,96	4,30	7,52
Găsit	71,03	4,15	7,22

Spectru IR (KBr): $\nu_{C=O} = 1670 \text{ cm}^{-1}$; $\nu_{C=O \text{ benzil}} = 1550 \text{ cm}^{-1}$.

Spectru RMN ($CDCl_3$): multiplet centrat $\delta = 7,34$ (14 H) protoni aromatici.

3.4. Anhidro-2-hidroxi-3-benzoil-7-metoxi-imidazolo-[2,1-b]-benztiazolium-hidroxiđ (9 b)

0,364 g (0,001 moli) bromură de N-fenacil-6-metoxi-benztiazoliu (1 b) se suspendă în 25 ml clorură de metilen. Se adaugă apoi 0,11 ml (0,001 moli) izocianat de fenil și 0,14 ml (0,0015 moli) trietilamină. Se lasă soluția 3 zile la temperatura camerei, se spală cu apă pentru îndepărtarea bromhidratului trietilaminei. Pulbere gălbuie p.t. 117°C (recristalizat benzen-eter de petrol).

Analize: $C_{23}H_{16}N_2SO_3$ (402)

	C%	H%	N%
Calculat	68,65	4,47	6,96
Găsit	68,61	4,20	6,62

Spectru IR (KBr): $\nu_{C=O}=1690\text{ cm}^{-1}$; $\nu_{C=O\text{ benzoil}}=1670\text{ cm}^{-1}$.

Spectru RMN ($CDCl_3$): singlet $\delta=3,8\text{ ppm}$ (3 H) OCH_3 ; triplet centrat $\delta=7,34\text{ ppm}$ (13 H) protoni aromatici.

3.5. 1-fenil-2-tio-3-benzoil-3,10 H-dihidroimidazolo-[2,1-b]-benztiazol (10)

0,34 g (0,001 moli) bromură de N-fenacil-benztiazoliu (1 a) se suspendă în 30 ml clorură de metilen. Se adaugă apoi 0,12 ml (0,001 moli) izocianat de fenil și 0,14 ml (0,0015 moli) trietilamină. După o încălzire de 5 min. se lasă la temperatura camerei 2...3 zile, se spală cu apă pentru îndepărtarea bromhidratului trietilaminei. Produs de culoare portocalie p.t. 148°C (recristalizat heptan-eter de petrol).

Analize: $C_{22}H_{16}N_2SO$ (388)

	C%	H%	N%
Calculat	68,04	4,12	7,21
Găsit	67,92	4,12	7,06

Spectru IR (KBr): $\nu_{C=O}=1690\text{ cm}^{-1}$; $\nu_{C=S}=1475\text{ cm}^{-1}$.

Spectru RMN ($CDCl_3$): singlet $\delta=4,40\text{ ppm}$ (1 H) H_a ; singlet $\delta=5,3\text{ ppm}$ (1 H) H_b ; multiplu centrat $\delta=7,4\text{ ppm}$ (14 H) protoni aromatici.

4. Concluzii

S-au obținut o serie de produși de ciclizare, prin închiderea unui inel de 5 atomi, ca urmare a reacțiilor de cicloadiție a benztiazoliu-ilidelor formate *in situ* la acetilendicarboxilat de metil, izocianat de fenil și izotiocianat de fenil.

Mecanismul reacției implică o cicloadiție 3+2 dipolară după un mecanism concertat.

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ACTION DES DIÉNOPHILES ACÉTYLÉNIQUES ET DE CERTAINES HÉTÉROCUMULÈNES SUR LES SELS DU N-PHÉNACYL- ET N-CARBÉTHOXYMÉTHYL-BENZOTHAZOLIUM

(Résumé)

On a obtenu une série de produits de cyclisation par la fermeture d'un anneau de 5 atomes par suite des réactions de cycloadditions des benzothiazolium-ylures formés *in situ* chez l'acétylène-dicarboxylate de méthyle, l'isocyanate de phényle et l'isothiocyanate de phényle.

Le mécanisme de la réaction implique une cycloaddition 3+2 dipolaire selon un mécanisme concerté.

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DÉRIVÉS DIPOLAIRES EN SÉRIE QUINAZOLINIQUE

II. SYNTHÈSE DE 1-BENZOYLE-3-(*p*-R-BENZOYLE)-PYRROLO/1,2-*c*/QUINAZOLINE

PAR

EMILIAN GEORGESCU, I. DRUȚĂ et MAGDA PETROVANU

1. Introduction

Dans le cadre des recherches concernant l'obtention et la réactivité des diazinium-ylures [1], nous avons montré que les quinazolinium-ylures *in situ* réagissent avec les alcynes, tels que l'acétylénedicarboxylate de méthyle et le propiolate d'éthyle, en conduisant à des adduits cycliques de structure pyrrolo/1,2-*c*/quinazolinique [2].

Comme on le sait, les alcynes sont, en général, de bons dipolarophiles, surtout lorsqu'ils sont conjugués. La littérature offre de nombreux exemples de leur réaction avec diverses familles de dipôles 1.3. Le problème de l'orientation de l'addition a tout particulièrement retenu l'attention des chercheurs vu qu'on ne peut pas prévoir *a priori* lequel des facteurs, électronique ou stérique, est celui qui dirige l'orientation de l'addition.

L'objet de la présente Note est d'approfondir le mécanisme et la stéréochimie de l'addition des quinazolinium-ylures (I *a...d*) à la phényléthynylène cétone, alcyne dissymétrique contenant le groupement benzoylique caractérisé par un puissant pouvoir électroattracteur.

2. Résultats et discussions

Dans un travail précédent on a constaté que les réactions de cycloadditions 3+2 dipolaires des quinazolinium-ylures aux alcynes ont lieu de la manière suivante : on fait réagir simultanément la quinazoline, un dérivé α -halogéno-carbonylique et un alcyne, en milieu basique.

Nous avons donc procédé de la même manière pour l'étude des réactions de cycloaddition des quinazolinium-ylures (I *a...d*) à la phényléthynylène-cétone. On a obtenu, dans les conditions expérimentales mentionnées ci-dessus, quatre adduits cycliques de structure 1-benzoyle-3-(*p*-R-benzoyle)-pyrrolo/1,2-*c*/quinazolinique (Tableau 1).

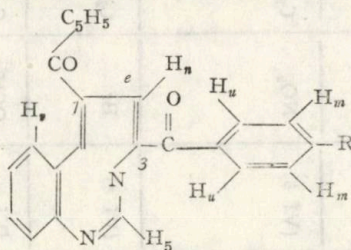
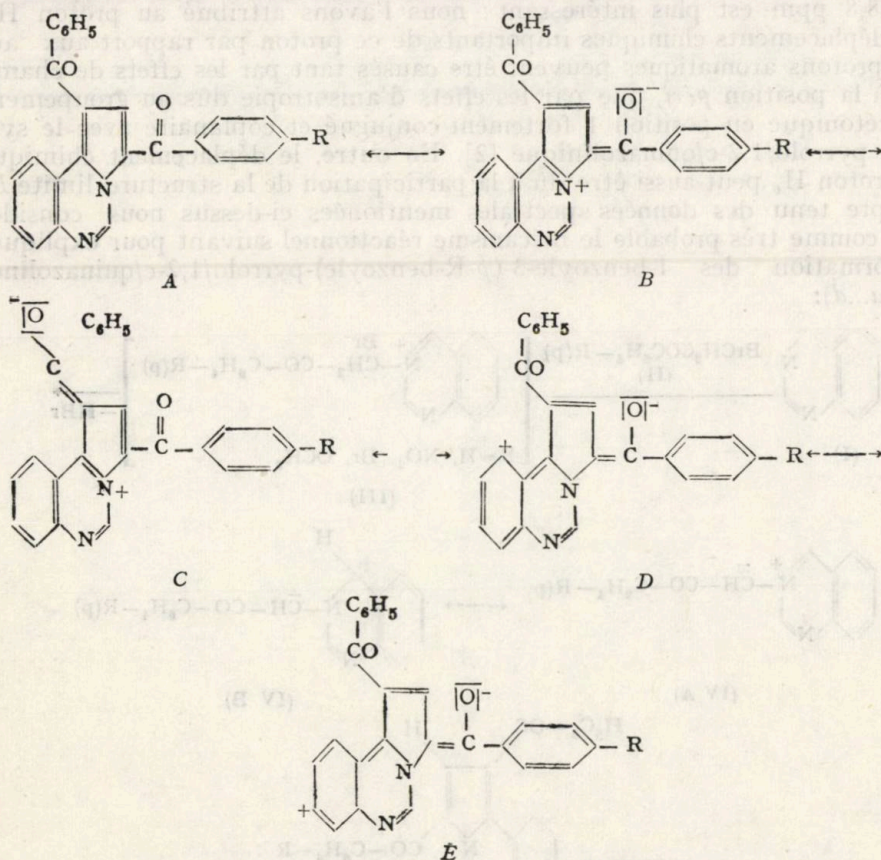


Tableau 1

Compo- sant	R	Formule	Analyse élémentaire			Spectre IR (KBr ν),	Spectre RMN (δ , TMS)
			Pro- duit	Cal- culé	Trou- vé		
(VI a)	H	$C_{25}H_{16}N_2O_2$ (376)	C% H% N%	79,78 4,25 7,45	79,63 4,41 7,63	1 640 cm^{-1} (CO cétonique-1) 1 620 cm^{-1} (CO cétonique-3)	(CDCl ₃) : multiplet 7,09 ... 7,9 ppm (14 H aromatiques) ; multiplet 8,6 ... 8,82 ppm (1H, <i>H_v</i>) ; singulet 10,5 ppm (1H, <i>H_s</i>).
(VI b)	NO ₂	$C_{25}H_{15}N_3O_4$ (421)	C% H% N%	71,26 3,56 9,97	69,97 3,43 10,12	1 643 cm^{-1} (Co cétonique-1) ; 1 622 cm^{-1} (CO cétonique-3) ; 1 523 cm^{-1} (NO ₂ asymétrique) 1 347 cm^{-1} (NO ₂ symétrique)	(DMSO) : multiplet 7,1 ... 7,92 ppm (12 H aromatiques parmi lesquelles à 7,85 ppm doublet (1 H, <i>H_u</i>), <i>J</i> =8,8 Hz) ; doublet 8,22 ppm (1H, <i>H_m</i>), <i>J</i> =8,8 Hz ; multi- plet 8,62 ... 8,82 ppm (1H, <i>H_v</i>) ; singulet 10,53 ppm (1 H, <i>H_s</i>).
(VI c)	Br	$C_{25}H_{15}N_2O_2Br$ (455)	C% H% N%	65,93 3,30 6,15	65,84 3,57 6,34	1 642 cm^{-1} (CO cétonique-1) 1 621 cm^{-1} (CO cétonique-3)	(CDCl ₃) : multiplet 7,08 ... 8 ppm (13 H aromatiques) ; multiplet 8,6 ... 8,83 ppm (1H, <i>H_v</i>) ; singulet 10,48 ppm (1H, <i>H_s</i>).
(VI d)	OCH ₃	$C_{26}H_{18}N_2O_3$ (406)	C% H% N%	76,85 4,43 6,90	76,70 4,61 7,12	1 639 cm^{-1} (CO cétonique-1) 1 621 cm^{-1} (CO cétonique-3) 1 170 cm^{-1} , 1 250 cm^{-1} (C—O—C)	(CDCl ₃) : singulet 3,77 ppm (3H, OCH ₃) ; multiplet 6,7 ... 7,95 ppm (13 H aroma- tiques parmi lesquels à 6,8 ppm doublet (1H, <i>H_m</i>), <i>J</i> =9 Hz) ; multiplet 8,63 ... 8,87 ppm (1H, <i>H_v</i>) ; singulet 10,4 ppm (1H, <i>H_s</i>)

La structure des adduits cyclyques (VI *a...d*) a été déterminée par voie chimique et spectrale. Ainsi dans les spectres IR des produits (VI *a...d*) les deux groupements CO cétoniques présentent des absorptions à des nombres d'ondes particulièrement bas. En général ces absorptions, situées entre $1\,620\text{ cm}^{-1}$ et $1\,643\text{ cm}^{-1}$, ne peuvent être expliquées que si l'on admet une participation importante des structures limites *B* et *C*.

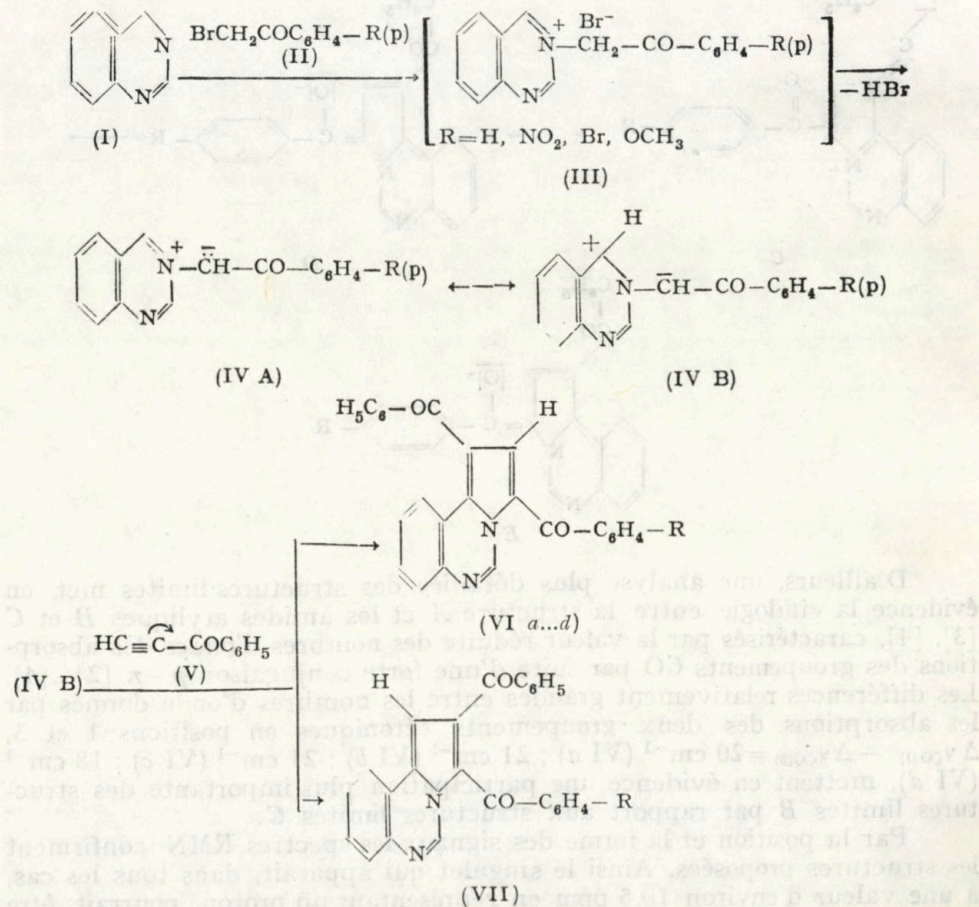


D'ailleurs, une analyse plus détaillée des structures limites met en évidence la vinilogie entre la structure *A* et les amides arylques *B* et *C* [3], [4], caractérisés par la valeur réduite des nombres d'ondes des absorptions des groupements CO par suite d'une forte conjugaison $p-\pi$ [2]...[4]. Les différences relativement grandes entre les nombres d'onde donnés par les absorptions des deux groupements cétoniques en positions 1 et 3, $\Delta\nu_{\text{CO}(1)} - \Delta\nu_{\text{CO}(3)} = 20\text{ cm}^{-1}$ (VI *a*) ; 21 cm^{-1} (VI *b*) ; 21 cm^{-1} (VI *c*) ; 18 cm^{-1} (VI *d*), mettent en évidence une participation plus importante des structures limites *B* par rapport aux structures limites *C*.

Par la position et la forme des signaux les spectres RMN confirment les structures proposées. Ainsi le singulet qui apparait, dans tous les cas, à une valeur d'environ $10,5\text{ ppm}$ en représentant un proton, pourrait être

attribué soit à H_5 soit à H_n . Mais, en conformité avec les résultats obtenus dans un travail antérieur [2] à l'aide des modèles, nous l'avons attribué, avec certitude, au proton H_5 . Le signal fourni par le proton H_n est difficile à identifier à cause de sa superposition avec les signaux des autres protons aromatiques.

Le multiplet qui apparaît, dans tous les cas, vers les valeurs de 8,6...8,8 ppm est plus intéressant; nous l'avons attribué au proton H_r . Les déplacements chimiques importants de ce proton par rapport aux autres protons aromatiques peuvent être causés tant par les effets de champ dûs à la position *péri*, que par les effets d'anisotropie dûs au groupement CO cétonique en position 1 fortement conjugué et coplanaire avec le système pyrrolo/1,2-c/quinazolinique [2]. En outre, le déplacement chimique du proton H_v peut aussi être dû à la participation de la structure limite D. Compte tenu des données spectrales mentionnées ci-dessus nous considérons comme très probable le mécanisme réactionnel suivant pour expliquer la formation des 1-benzoyle-3-(*p*-R-benzoyle)-pyrrolo/1,2-c/quinazolines (VI a...d):



Comme on le voit dans le schéma ci-dessus on admet la formation initiale des sels de cycloimmonium ((III), $R=H$; NO_2 ; Br ; OCH_3) qui en milieu alcalin subissent une déhydrobromuration et donnent naissance aux quinazolinium-ylures correspondants (VI A, B).

Comme tous les cycloimmonium-ylures, les quinazolinium-ylures admettent à côté d'une structure „octet“ (VI A), une structure „sextet“ de dipôle 1, 3 (VI B). Grâce à cette structure (IV B) ces ylures réagissent avec les agents dipolarophyles présents dans le mélange réactionnel (dans notre cas la phényle-éthynyle cétone (V). Lorsque l'agent dipolarophyle est dissymétrique l'addition peut conduire à deux adduits cycliques, par suite des deux sens d'addition possibles. Dans notre cas l'addition pouvait conduire à deux adduits cycliques (VI) et (VII).

Dans les produits de type (VI) le carbanion ylurique est lié à l'atome de carbone positif du dipolarophyle, c'est à dire l'addition à lieu dans le sens favorisé par les facteurs électroniques.

Par contre, une structure de type (VII) prendrait naissance par suite d'une addition inverse à la première. Les données analytiques et spectrales plaident en faveur des structures (VI a...d).

On peut donc conclure qu'un seul sens d'addition a été observé, précisément celui favorisé par les facteurs électroniques.

3. Partie expérimentale

Les points de fusion ne sont pas corrigés. Les spectres RMN ont été enregistrés sur un spectromètre de type JEOL 60 Mc et les spectres IR sur un spectromètre de type UR-20.

a) 1,3-Dibenzoyl-pyrrolo[1,2-c]quinazoline (VI a)

On dissout 1,3 g (10 mmol) de quinazoline et 1,99 g (10 mmol) de bromure de phénacyle dans 50 ml de propène oxyde, on ajoute 1,3 g (10 mmol) de phényle-éthynyle-cétone et on agite pendant 50 h à la température ambiante. On évapore le solvant et on reprend le résidu avec de l'acétone chaude. Par refroidissement de la solution acétonique on obtient des cristaux jaunes à p.f. 202,5°...203,5°C. Rendement total : 1,25 g (33,24%).

b) 1-Benzoyl-3-(4'-nitro-benzoyl)-pyrrolo[1,2-c]quinazoline (VI b)

On dissout 1,3 g (10 mmol) de quinazoline et 2,44 g (10 mmol) de bromure de *p*-nitrophénacyle dans 50 ml de propène oxyde, on ajoute 1,3 g (10 mmol) de phényle-éthynyle-cétone et on agite pendant 50 h à la température ambiante. On évapore une partie du solvant et on abandonne au réfrigérateur pendant 3 h. On filtre le précipité obtenu et on le recristallise dans du chloroforme. On obtient 0,85 g de cristaux jaunes à p.f. 251,5°...252°C. On récupère encore du filtrat 1,13 g produit. Rendement total : 1,98 g (47%).

c) 1-Benzoyl-3-(4'-bromobenzoyl)-pyrrolo[1,2-c]quinazoline (VI c)

On dissout 1,3 g (10 mmol) de quinazoline et 2,78 g (10 mmol) de bromure de *p*-bromophénacyle dans 50 ml de propène oxyde, on ajoute 1,3 g (10 mmol) de phényle-éthynyle-cétone et on agite pendant 50 h à la température ambiante. On évapore une partie du solvant et on abandonne au réfrigérateur pendant la nuit. On filtre le précipité obtenu et on le recristallise dans un mélange chloroforme-éther éthylique. On obtient 0,67 g de cristaux jaune pâles à p.f. 200°...201°C. On récupère encore du filtrat 1,1 g produit. Rendement total : 1,77 g (38,9%).

d) 1-Benzoyl-3-(4'-méthoxy-benzoyl)-pyrrolo[1,2-c]quinazoline (VI d)

On dissout 1,3 g (10 mmol) de quinazoline et 2,3 g (10 mmol) de bromure de 4-méthoxyphénacyle dans 50 ml de propène oxyde, on ajoute 1,3 g (10 mmol) de phényle-éthynyle-cétone et

on agite pendant 50 h à la température ambiante. On évapore 3/4 parts du solvant, on ajoute de l'acétone, on abandonne au réfrigérateur pendant 2 h et on filtre le précipité obtenu. Après recristallisation dans un mélange chloroforme-éther éthylique on obtient 1,31 g de cristaux aciculaires jaunes pâles à p.f. 194°...195,5°C. Rendement total: 32,26%.

Requ le 20 octobre 1980

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DERIVAȚI DIPOLARI ÎN SERIA CHINAZOLINEI I

II. Sinteza 1-benzoil-3-(*p*-R-benzoil)-pirolo[1,2-*c*]chinazolinei

(Rezumat)

În cadrul unor cercetări privind obținerea și reactivitatea unor compuși dipolari în seria chinazolinei am studiat și reacțiile unor chinazolinu-ilide (IV) *in situ* cu unele alcine disimetrice ca de exemplu fenil-etinil-cetona. Cicloaducții (VI a....d) au fost caracterizate prin analize chimice și spectrale (IR, RMN).

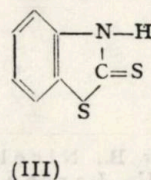
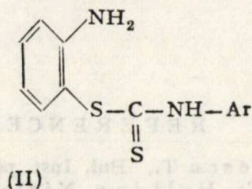
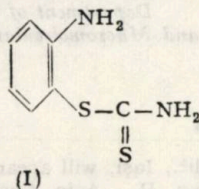
REACTION BETWEEN *o*-AMINOTHIOPHENOL AND ISOTHIOCYANIC ACID (II)

BY

TATIANA NICOLAESCU and BORIS ARVENTIEV

1. Introduction

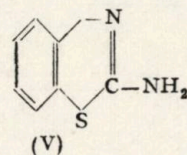
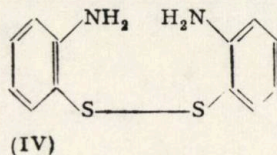
In a previous paper [1] the reaction between *o*-aminothiophenol and isothiocyanic acid starting from *o*-aminothiophenol and kalium thiocyanate, in acetic acid at different temperatures was reported. For the addition product obtained at the room temperature the structure (I) might be supposed by analogy with the addition products between *o*-aminothiophenol and aryl isothiocyanate (II) ($\text{Ar} = \text{C}_6\text{H}_5^1$, *m*-tolyl, *o*-tolyl). [3]:



By heating for 8...9 hours on steam bath the 2-benzothiazolinthione (III) was obtained.

2. Results and Discussion

In the present paper other products formed in these reactions are also separated. Thus, after separating the addition product (I) formed at the room temperature, 2,2'-diaminodiphenyldisulfide (IV) and (I) was separated chromatographically. In case of the reaction carried out by heating on steam bath, the product (IV) and 2-amino-benzthiazole (V) were also separated chromatographically:



¹) The addition products between *o*-aminothiophenol and phenyl isothiocyanate has been prepared before us by Uffe Anthoni and others [2].

3. Experimental

a) *o*-Aminothiophenol and Isothiocyanic Acid in Acetic Acid at the Room Temperature

2.7 g *o*-aminothiophenol and 4.1 g kalium thiocyanate are solved in 4 ml acetic acid and 2 ml water at the room temperature. After 72 hours a product separates with melting point (m.p.) 122°...130°C [1]. The product separated from the following fractions (m.p. 110°...140°C) is then chromatographed on a silicagels column (30...70 mesh) of 50 cm length and 22 mm diameter. 0.5 g of product are solved in warm CS₂. By elution with petroleum ether—benzene mixture followed by benzene : methanol mixture (8 : 2) the *o*-aminodiphenyldisulfide (the IR spectrum is identical with the literature one) and the addition product (I) (m.p. = 132°C) are separated, respectively.

b) *o*-Aminothiophenol and Isothiocyanic Acid by Heating on Steam Bath

2.5 g *o*-aminothiophenol and 2 g kalium thiocyanate are solved in 10 ml of hot glacial acetic acid and the solution boiled for 8...9 hours on steam bath. By cooling the reaction product separates (mercaptobenzthiazole, m.p. = 179°C) which was identified and characterized [1].

From the filtrate a product melting at 90°...100° separates which is chromatographed on a column identical with that previously mentioned. 0.5 g of substance are solved in hot CS₂. The first product separated by elution with petroleum ether—benzene mixture (1 : 1) is the *o*-amino-phenyldisulfide whose melting point and IR spectrum are identical with literature ones. The second product, 2-amino-benzthiazole, was separated with benzen—acetone mixture (95 : 5). The melting point (128°C) and the IR spectrum are identical with the literature ones.

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REAȚIA DINTRE *o*-AMINOTIOFENOL ȘI ACID IZOTIOCIANIC (II)

(Rezumat)

Se continuă izolarea și a altor produși formați în reacțiile dintre *o*-aminotiofenol și acid izotiocianic. Astfel, în reacția la temperatura camerei s-au mai izolat cromatografic 2,2-diaminodifenil-disulfura (IV) și (I). În reacția la încălzire pe baie de apă s-au mai izolat cromatografic (IV) și (V).

THERMOGRAVIMETRICAL CHARACTERIZATION OF POLYVINYLACETATE (PVA) SYNTHESISED IN THE PRESENCE OF SEPHADEX G-10

BY

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1. Introduction

The requirement of obtaining some macromolecular compounds with stereospecific structure and thus with higher physical and mechanical properties led to the matrix polymerization [1].

Various theories are reported in the literature; among them the well known „lock and key“ theory developed for explaining both the ability of cyclodextrins to form inclusion products with a large variety of organic and inorganic substances [3] and the induced catalysis of certain reactions [4], [5].

In this connection, the ability of cyclodextrins to form inclusion products with various aliphatic and aromatic compounds of suitable sizes suggested the use of Sephadex for obtaining new polymers [6].

The Sephadex G-50 obtained from partially hydrolysed dextrin [7], [8], by crosslinking some fractions with epichlorohydrin in the presence of sodium hydroxide and forming of glyceric bridges between dextrin chains, exhibits a granular regular structure, while the existence of cavities characteristic to cyclodextrins argues for its use in matrix polymerization [10].

In the present paper a thermogravimetric study regarding the polymerization of vinylacetate (guest) in the presence of Sephadex G-50 gel (host) is accomplished, the influence of reaction parameters on thermostability being followed.

2. Experimental

Sephadex G-50 (Uppsala, Sweden) and vinyl acetate (VA) (Schuchardt, München) of high purity were used.

The photopolymerization of vinylacetate was accomplished in inert medium by initiating with UV radiations emitted by a Hg vapours lamp ($P=500$ W), the influence of temperature, time and Sephadex to VA ratio on the polymerization yield and thermal stability being followed.

The freshly distilled monomer was added to Sephadex gel in aqueous medium (weight ratio water to Sephadex=10/1).

The polymer separation from support was carried out by dissolving in methanol, filtrating and reprecipitating with excess water. The purification was accomplished by repeated filtrations and reprecipitating with excess water, the product being dried under vacuum at 30°C.

3. Results and Discussion

Series of experiences varied out between -27°C and $+7^{\circ}\text{C}$, at durations of 3.3...6.7 h with Sephadex to VA ratios comprised between 2.15...3.84 showed the best results to be obtained at a reaction duration of 5 h, with Sephadex to VA ratios of 2.5...3 (fig. 1 a, b).

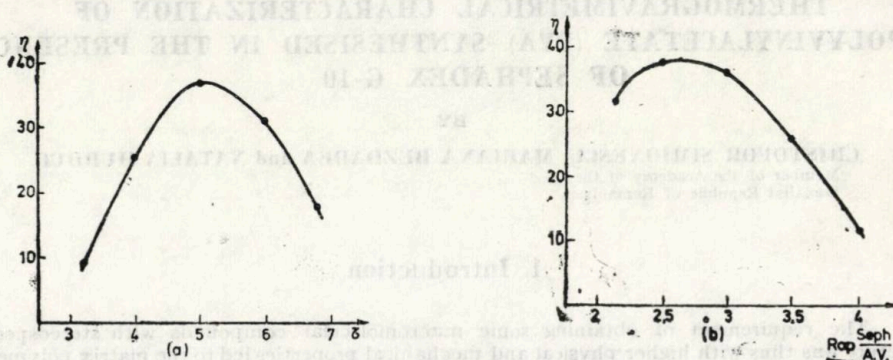


Fig. 1. — Influence of reaction duration on the yield (a); influence of Sephadex to VA ratio on the reaction yield (b).

In fig. 2 the influence of temperature on the yield of polymerization reaction, at constant values of other parameters (5 h reaction duration, Sephadex/VA ratio=3) is represented. The increased amount of polymer can be correlated with increasing reaction rate with temperature (Fig. 2).

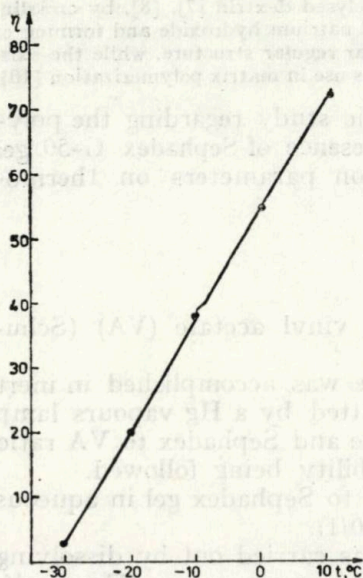


Fig. 2. — Influence of polymerization temperature on the yield.

The synthesised samples were characterized by thermogravimetical analysis.

The thermograms were recorded in air, at a heating rate of $12^{\circ}\text{C}/\text{min}$ on a MOM, Budapest, type derivatograph.

Thermograms of the samples synthesised under the same temperature conditions (-10°C) and Sephadex to VA ratios of 3, and for various reaction durations are given in Figs. 3...6.

A similar behaviour is noticed as regards the complete degradation up to 600°C , in three stages, and the weight losses.

The thermogravimetical features and the apparent energy of activation, estimated by the differential F.C. method [9], are given in Table 1, compared to a standard PVA_c sample with an overall activation energy of 184 KJ/mole.

The kinetic parameters do not indicate significant changes during 3...5 h range, the thermostabilities being comparable. The activation ener-

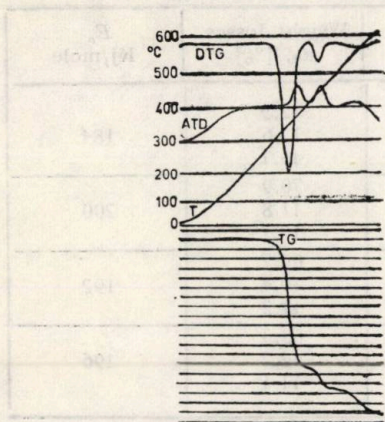


Fig. 3. — Thermogram
PVA₆: ind. B.D.H.

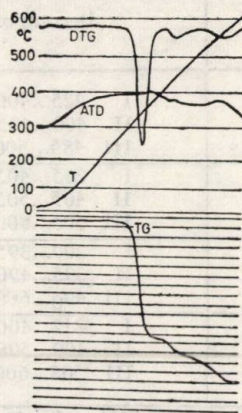


Fig. 4. — 21 polymer-
ized sample, $t = -10^{\circ}\text{C}$,
duration 5 h, Sepha-
dex/VA ratio=3.

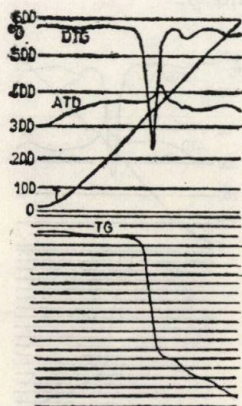


Fig. 5. — 11 polymer-
ized sample, $t = -10^{\circ}\text{C}$,
duration 3.25 h, Sepha-
dex/VA ratio=3.

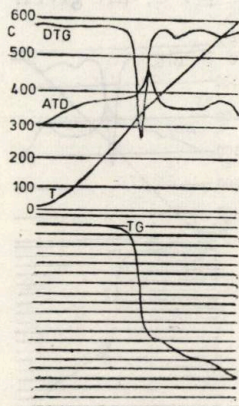


Fig. 6. — 12 polymer-
ized sample, $t = -10^{\circ}\text{C}$,
duration=6.44 h, Sepha-
dex/VA ratio=3.

gies varie between 184 and 200 KJ/mole. Taking into account the thermostability and the yield, the optimum reaction time seems to be of 5 h. The decrease of polymer yield with increasing reaction duration can be accounted for by the occurrence of some degrading processes under the influence of UV radiations.

As a next step the influence of temperature was investigated, working at the optimum durations and Sephadex to VA ratio. The recorded

Table 1
Thermogravimetric Characteristics and Apparent Activation Energies, Estimated by F.C. Differential Method, Compared to a Standard PVAc Sample

Sample	Decomposing range °C	Weight losses, w_i , [%]	E_a KJ/mole
ind. PVAc BDH	I 225...400	72,5	184
	II 400...485	12,6	
	III 485...600	13,1	
11	I 205...405	70,9	200
	II 405...505	11,8	
	III 505...600	10,7	
21	I 200...395	69,7	192
	II 395...490	10,4	
	III 490...600	12,2	
12	I 212...400	68,3	196
	II 400...508	12,2	
	III 508...600	11,1	

Industrial PVAc, The British drug Houses LTD. England

11 — polymerized sample: duration = 3,26 h, $t = -10^\circ\text{C}$ and Sephadex/VA ratio = 3;

21 — polymerized sample: duration = 5 h, $t = -10^\circ\text{C}$ and Sephadex/VA ratio = 3;

12 — polymerized sample: duration = 6,44 h, $t = -10^\circ\text{C}$ and Sephadex/VA ratio = 3.

thermograms for PVA_e synthesised at temperatures varying between -13°C and $+7^\circ\text{C}$, are given in Figs. 4, 7 and 8.

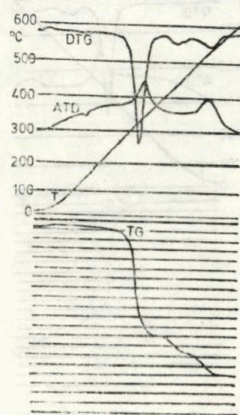


Fig. 7. — 23 polymerized sample; $t = -13,5^\circ\text{C}$, duration = 5 h, Sephadex/VA ratio = 3.

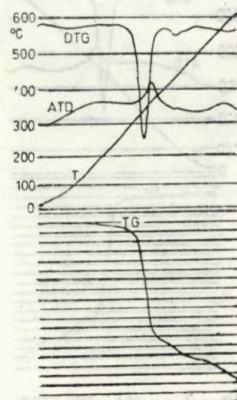


Fig. 8. — 10 polymerized sample, $t = +7,3^\circ\text{C}$, duration = 5 h, Sephadex/VA ratio = 3.

The thermogravimetric characteristics are given in Table 2. The obtained data suggests the increase of thermostability with decreasing temperature. The sample synthesised at -10°C has a behaviour similar to that of standard polymer. When the polymerization was carried out at -13°C , an increase of thermostability occurred, determined, probably, by the increased degree of ordering within the system.

Table 2

Thermogravimetric Characteristics and Apparent Activation Energy, as Functions of Polymerization Temperature

Sample	Temperature range °C	Weight losses W%	E_a Kj/mole
21	I 200...395	69.7	192
	II 395...490	10.4	
	III 490...600	12.2	
23	I 200...390	69.5	212
	II 390...480	12.1	
	III 480...600	12.1	
10	I 200...400	68,5	171
	II 400...515	11,04	
	III 515...600	11,04	

21 — polymerized sample, $t = -10^\circ\text{C}$, duration = 5 h and Sephadex/VA ratio = 3

23 — polymerized sample, $t = -13,5^\circ\text{C}$, duration = 5 h and Sephadex/VA ratio = 3

10 — polymerized sample, $t = +7,3^\circ\text{C}$, duration = 5 h and Sephadex/VA ratio = 3.

4. Conclusions

The thermogravimetric study under dynamic temperature conditions lead to the finding of optimum synthesis conditions for matrix polymerization of vinylacetate by photochemical initiation: duration = 5 h, temperature = -13°C , Sephadex/VA ratio = 3.

The thermostability was found to increase with decreasing synthesis temperature which suggested the increase of crystallinity degree of the system and of the stereospecificity, respectively.

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SYNTHESIS AND PROPERTIES OF SOME NEW POLYAZOMETHINES

POLYACENAPHTHENEQUINONIMINE

BY

TATIANA LIXANDRU, MARIANA PĂSTRĂVANU and MARIA DUMITRIU

1. Introduction

The heterochain polymers show important properties connected with their structure and the presence of the heteroatom in the molecule (thermal stability, semiconducting, catalytical and photosensitive properties, etc.) which determines their use in numerous fields.

The α -dicarbonylic components are particularly interesting in obtaining polyazomethine since they lead to conjugated systems.

In the present paper the synthesis and properties of new polyazomethines derived from acenaphthenequinone and its derivatives is reported.

2. Experimental

1. 1. Materials

a) Acenaphthenequinone, Merck-Schuchardt product, m.p. = 248°....
...253°C. Recrystallized from *m*-xylene, m.p. = 261°C.

b) 5-Chloracenaphthenequinone was synthesized by 5-chloroacenaphthene oxydation [1]. After recrystallization from acetic acid/water the pure product melted at 218°C.

c) 5-Nitro- and 5,6-dinitroacenaphthenequinone were prepared by acenaphthenequinone nitration [2], [3]. After recrystallization from acetic acid, m.p. = 218°C and 300°C for the 5-nitro and 5,6-dinitro derivatives, respectively.

d) *p*- and *m*-Phenylenediamine, Fluka AG products, after recrystallization from ethanol m.p. = 147°C for *p*-phenylenediamine and 64°C for *m*-phenylenediamine.

The IR and RES spectra were recorded on a Specord-71 and ART-5 apparatus, respectively. The thermograms were obtained with a J. Paulik — F. Paulik — L. Erdely, MOM, Budapest, apparatus.

2. 2. Polycondensation Procedure

0.05 mole quinone and 0.05 mole diamine is solved in 40 ml solvent, refluxed under stirring for 5 hours, then cooled and filtered. The crude

product are purified by repeated washing with hot glacial acetic acid, xylene and ethanol to remove the unreacted reagents. Some characteristic of the synthesized products are listed in Table 1.

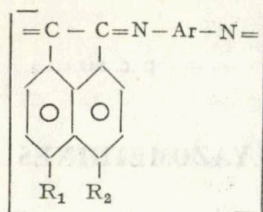


Table 1

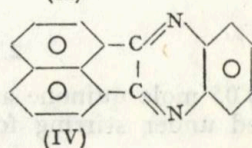
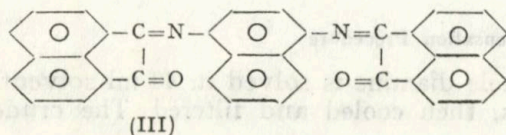
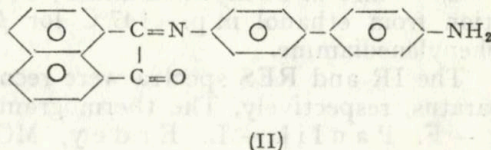
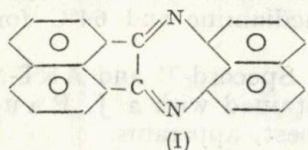
Characteristics of Polyacenaphthenequinonimines

R ₁	R ₂	Ar	Solvent	Yield %	Melting point °C	Aspect	IR absorptions ν _{C=N} cm ⁻¹
H	H	<i>p</i> -C ₆ H ₄ -	acetic acid	49.37	>365	Amorphous, brown-red	1650
H	H	<i>m</i> -C ₆ H ₄ -	acetic acid	66.90	>365	Amorphous, brown-red	1650
H	H	<i>p</i> -C ₆ H ₄ -	<i>p</i> -xylene	82.16	>365	Amorphous, brown-red	1660
H	H	<i>m</i> -C ₆ H ₄ -	<i>p</i> -xylene	78.93	>365	Amorphous, brown-red	1668
H	Cl	<i>p</i> -C ₆ H ₄ -	acetic acid	34.00	260	Amorphous, brown	1650
H	Cl	<i>m</i> -C ₆ H ₄ -	acetic acid	67.54	>290	Amorphous, dark-brown	1620
H	Cl	<i>p</i> -C ₆ H ₄ -	<i>p</i> -xylene	89.45	>290	Amorphous, dark-brown	1630
H	Cl	<i>m</i> -C ₆ H ₄ -	<i>p</i> -xylene	49.70	>290	Amorphous, black	1630
H	NO ₂	<i>p</i> -C ₆ H ₄ -	acetic acid	40.00	288	Amorphous, light-brown	1680
H	NO ₂	<i>m</i> -C ₆ H ₄ -	acetic acid	73.56	>280	Amorphous, light-brown	1680
H	NO ₂	<i>p</i> -C ₆ H ₄ -	<i>p</i> -xylene	75.20	>295	Amorphous, black	1650
H	NO ₂	<i>m</i> -C ₆ H ₄ -	<i>p</i> -xylene	83.50	>280	Amorphous, dark-brown	1650
NO ₂	NO ₂	<i>p</i> -C ₆ H ₄ -	acetic acid	46.20	>290	Amorphous, black	1680
NO ₂	NO ₂	<i>m</i> -C ₆ H ₄ -	acetic acid	66.62	>290	Amorphous, black	1680
NO ₂	NO ₂	<i>p</i> -C ₆ H ₄ -	<i>p</i> -xylene	91.45	>365	Amorphous, black	1650
NO ₂	NO ₂	<i>m</i> -C ₆ H ₄ -	<i>p</i> -xylene	64.49	>290	Amorphous, dark-brown	1650

3. Results and Discussion

3.1. Synthesis and Molecular Structure of the Polymers

The reaction of acenaphthenequinone and its substituted derivatives with aromatic diamines leads to either mono- and bisazomethines (I), (II) [4] or cyclization derivatives of the types (III) and (IV) [5]...[12].



Since acenaphthenequinone and phenylenediamines are bifunctional components the formation of macromolecular compounds is also possible.

By carrying out the polycondensation under different conditions the parameters for obtaining polyacenaphthenequinonimines were established. The reaction was carried out in both protic (acetic acid) and aprotic (*p*-xylene) solvent at a 1/1 mole ratio and duration of 5 hours. Insoluble, amorphous, dark-coloured and high melting ((280°...365°C) polymers were thus obtained (Table 1).

The obtained yields are dependent on the solvent nature being higher with *p*-xylene. This fact might be explained by decrease in the nucleophilic power of the amino groups as a consequence of their protonation and partial blocking by acetylation (the IR spectra show absorption bands characteristics of the terminal acetyl residues).

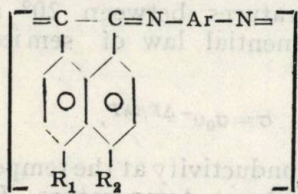
As regards the diaminic component, higher yields are noticed with *m*-phenylenediamine than with *p*-phenylenediamine, a few exceptions only being observed. These results are in good agreement with those reported by d'Alerio for the melt polycondensation of isophthalaldehyde with *m*- and *p*-phenylenediamine [13].

The molecular weights and intrinsic viscosities of the polymer could not be determined due to their insolubility in most organic solvents. The molecular weight could be determined (osmometrically in DMSO) only for the polyazomethine of acenaphthenequinone with *m*-phenylenediamine synthesized in acetic acid ($M=5\,950$) and in *p*-xylene ($M=1\,030$).

The polyacenaphthenequinonimines structure was attributed based on both elemental analysis data and IR spectral measurements. All IR spectra showed absorptions characteristic of the $\nu_{C=N}$ valence vibrations between $1\,620$ and $1\,680\text{ cm}^{-1}$, the position of the band depending on the nature of substituent (Table 1). The characteristic bands for $C=O$ and $N-H$ bond valence vibrations indicate the presence of the terminal carbonylic and aminic groups. For the polyacenaphthenequinonimines synthesized in acetic acid the spectra exhibited bands at $1\,560\text{ cm}^{-1}$ (amide II), $1\,700\text{ cm}^{-1}$ (amide I) and $2\,850\text{--}2\,950\text{ cm}^{-1}$ (sym. and asym. $C-H$ in CH_3) which are indicative of acylation of the terminal amino groups.

The bands characteristics of the aromatic ring and of the substituents in dicarbonylic component are found in all spectra ($1\,340\text{ cm}^{-1}$ for $\nu_{NO_2\text{sym}}$ and $1\,530\text{ cm}^{-1}$ for $\nu_{NO_2\text{asym}}$).

The IR spectra and elemental analysis data confirmed the polyazomethinic structure supposed for the synthesized polymers:



$R_1, R_2 = H,$

$R_1 = H; R_2 = Cl,$

$R_1 = H; R_2 = NO_2,$

$R_1 = NO_2; R_2 = NO_2,$

$Ar = m\text{-}C_6H_4\text{---}, \quad p\text{-}C_6H_4\text{---}$

The polycondensation reaction involves a nucleophilic addition followed by elimination. The initial nucleophilic attack at one of the carbon-

Table 2
Thermal Properties of Polyacenaphthenequinonimines

Polymer	T_d °C	Stages of thermal degradation								
		I			II			III		
		Temperature range °C	T_I °C	Weight losses %	Temperature range °C	T_{II} °C	Weight losses %	Temperature range °C	T_{III} °C	Weight losses %
Polyazomethines from: Acenaphthenequinone and <i>m</i> -phenylenediamine in acetic acid	272	272...403	370	8.57	403...732	543	82.6	—	—	—
Acenaphthenequinone and <i>p</i> -phenylenediamine in acetic acid	280	280...357	305	5.2	357...410	380	4.7	443...905	710	73.5
Acenaphthenequinone and <i>p</i> -phenylenediamine in <i>p</i> -xylene	383	383...759	595	79.2	759...880	800	20.8	—	—	—
5-Chloro-acenaphthenequinone and <i>p</i> -phenylenediamine in acetic acid	224	224...372	328	12.9	372...447	400	6.6	447...807	565	75.3
5-Nitro-acenaphthenequinone and <i>p</i> -phenylenediamine in xylene	270	270...759	570	96.5	—	—	—	—	—	—
5,6-Dinitro-acenaphthenequinone and <i>p</i> -phenylenediamine in acetic acid	270	270...440	400	20.1	440...726	560	72.4	—	—	—

T — initial temperature of weight loss; T_I , T_{II} , T_{III} , — temperature of exothermic point observed by differential thermal analysis in air, (from DTG curves).

By comparing the electrophysical properties of polyazomethines from acenaphthenequinone and its substituted derivatives (Table 3) with the corresponding polyazine [15] it appears that the introducing of the aryl residue between the nitrogen atoms increases the electrical conductivity ($\sigma = 10^{-11} \dots 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$ and $\sigma = 10^{-15} \dots 10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$, respectively), the paramagnetic properties being not altered.

The electrical conductivity is higher than those of polydiphenylen-azomethines, for which $\sigma_{400^\circ K} = 2 \times 10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$ [18] and of the poly-azomethines of benzyl or terephthalaldehyde, with $\sigma_{293^\circ K} = 3 \times 10^{-12} \dots 2 \times 10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$ [19].

Table 3
Electrophysical Characteristics of Polyacenaphthenequinonimines

No.	R ₁	R ₂	Ar	Solvent]	σ_{55° ohm ⁻¹ cm ⁻¹	ΔE eV	Concentration of unpaired electrons spin/g
1	H	H	<i>p</i> -C ₆ H ₄ —	acetic acid	5.78×10^{-10}	0.422	8.31×10^{20}
2	H	H	<i>p</i> -C ₆ H ₄ —	<i>p</i> -xylene	3.18×10^{-10}	0.381	—
3	H	H	<i>m</i> -C ₆ H ₄ —	<i>p</i> -xylene	3.43×10^{-11}	0.804	1.19×10^{20}
4	H	Cl	<i>p</i> -C ₆ H ₄ —	<i>p</i> -xylene	4.76×10^{-10}	1.309	4.86×10^{20}
5	H	Cl	<i>m</i> -C ₆ H ₄ —	<i>p</i> -xylene	2.63×10^{-10}	0.945	6.11×10^{21}
6	H	Cl	<i>m</i> -C ₆ H ₄ —	acetic acid	2.64×10^{-11}	0.420	9.48×10^{21}
7	NO ₂	NO ₂	<i>p</i> -C ₆ H ₄ —	<i>p</i> -xylene	4.37×10^{-11}	0.190	6.20×10^{21}
8	NO ₂	NO ₂	<i>m</i> -C ₆ H ₄ —	<i>p</i> -xylene	2.86×10^{-11}	0.342	8.66×10^{21}
9	H	H	<i>m</i> -C ₆ H ₄ —	acetic acid	—	—	1.30×10^{22}
10	H	NO ₂	<i>p</i> -C ₆ H ₅	acetic acid	—	—	2.32×10^{20}

4. Conclusions

The polycondensation of acenaphthenequinone and its substituted derivatives with *m*- and *p*-phenylenediamine leads to amorphous, coloured polyacenaphthenequinonimines, most of them being insoluble in the common organic solvents. The obtained polymers show a high thermal stability and semiconducting properties (electrical conductivity of the $10^{-11} \dots 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$ order and paramagnetic particle concentration of $10^{20} \dots 10^{22} \text{ spin/g}$).

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SINTEZA ȘI PROPRIETĂȚILE UNOR NOI POLIAZOMETINE

Poliacenaftenchinonimine

(Rezumat)

S-au sintetizat o serie de noi poliazometine prin reacția de policondensare a *m*- și *p*-fenilendiaminei cu acenaftenchinona, 5-cloracenaftenchinona, 5-nitroacenaftenchinona și 5,6-dinitroacenaftenchinona în acid acetic și *p*-xilen. Poliazometinele prezintă o foarte bună stabilitate termică și proprietăți semiconductoare ($\sigma = 10^{-11} \dots 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$; concentrație în particule paramagnetice de ordinul $10^{20} \dots 10^{22} \text{ spini/g}$).

CATALYSIS BY POLYMERS

II. SYNTHESIS OF 3-CHLORO-2-HYDROXI-PROPYL ACRYLATE USING
POLY(METHYLENE-N,N-DIMETHYLPYPERIDINIUM CHLORIDE) AS CATALYST

BY

SPIRIDON OPREA, EMIL DUMITRIU, LAURENȚIA ȘTEFĂNEL and V. HULEA

1. Introduction

As it is shown in the previous paper [1] the polymers having ionizable functions, as quaternary ammonium groups, present an important catalytic activity speeding up the esterification reaction of acrylic acid with epichlorohydrin. Studying the same reaction but in the presence of micromolecular quaternary compounds, Yoshio [2] found that the nature of substituents influences the catalytic efficiency. Certainly, the problem of substituents interests even in the case of polymers having the quaternary ammonium functions in the side chains.

Therefore in the present work the poly(methylene-N,N-dimethylpyperidinium chloride), polymer obtained by cyclopolymerization of a quaternary ammonium salt — dimethyldiallylammonium chloride, was used as catalyst for the mentioned reaction. This polymer was chosen as catalyst in the synthesis of 3-chloro-2-hydroxypropyl acrylate on the basis of two reasons: a) the monomer used for the polymer synthesis can also be used as catalyst, and b) the copolymers of diallylamine derivatives (quaternized derivatives) have demonstrated spectacular catalytic activities in a series of reactions in the aqueous medium as the reaction of the thio-sulphate with sodium chloroacetate, the aromatic nucleophil substitution reaction of 3,5-dinitro-4-chlorobenzoate, the reaction of 2,4-dinitrofluorobenzene with aminoacids and peptides, and others [3]. In the our case there is the possibility to study the catalytic activity of an homopolymer of the diallylamine derivatives type in an organic medium, fact which constitutes an interesting aspect of the behaviour of such a polymer.

2. Experimental

The epichlorohydrin and acrylic acid were purified in the same manner as in the previous paper [1]. The investigated polymer as catalyst was synthesised by the cyclopolymerization of dimethyldiallylammonium chloride using ammonium persulphate as initiator [4], [5]:

are fitted on the straight lines (at 55°C and 0...300 min., as time range) while at the polymer concentration of 10% a slight curvature appears, fact which would indicate either a tendency of saturation of the catalyst or the possibility of the existence of some interactions in the system (evidently, in the hypothesis that a certain reaction mechanism) is maintained.

If one takes into account the experimental data obtained in the presence of poly(dimethylaminoethyl methacrylate) quaternized with methyl iodide [1] seemingly the polymer used in this study would present an activity about twice more stronger at the same concentration in the system (e.g., for poly(methylene-N,N-dimethylpiperidinium chloride) at 55°C and 10% polymer the conversions are 27.52% at 135 min. and respectively 47.15% at 270 min. and for quaternized polymethacrylate the conversions are 12.56%, respectively 25.04%; the conversion ratio for the two polymers are 2.18, respectively 1.88. In fact, the poly(methylene-N,N-dimethylpiperidinium chloride) shows a higher catalytic activity but it is not so much as it seems because the molecular weight of its structural unit is 1.74 smaller than the molecular weight of the average unit of quaternized poly(dimethylaminoethyl methacrylate). On the basis of these experiments we can conclude that the polymer structure has a certain influence on the catalytic activity of the polymers even if in our case this is not too strong.

Further, maintaining the same ratio between reactants (acrylic acid : epichlorohydrin 1 : 1) and the same polymer concentration (5%) it was

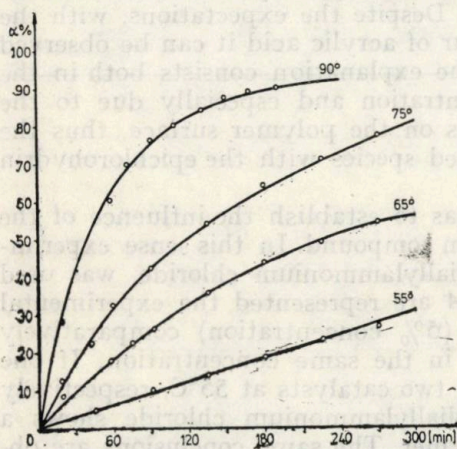


Fig. 2. — Conversion of acid against the time at different reaction temperatures; molar ratio 1:1; catalyst concentration 5%.

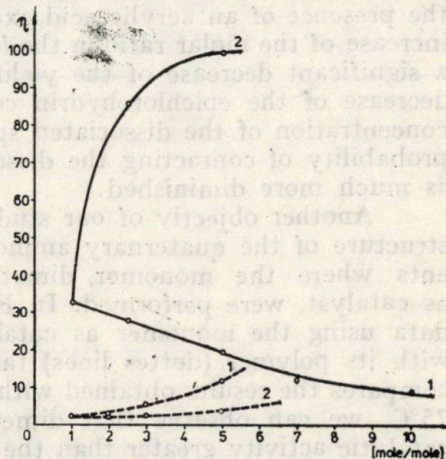


Fig. 3. — Yield against the molar ratio between the reactants; reaction temperature 70°C; catalyst concentration 5%; 1 — molar ratio acid; epichlorohydrin, 2 — molar ratio epichlorohydrin : acid, — in presence of the catalyst, --- without catalyst.

studied the influence of temperature on the esterification reaction (Fig. 2). As in previous case [1] one may find the same strong influence of temperature upon the esterification process. The temperature rising deter-

mines the increasing of conversion but as the first observation one may notice a more stronger curvature of the experimental curve which describe the variation of conversion against the time. Moreover the curve obtained at 90°C tends asimptotically to a limit value of the conversion of about 90%. The experimental data obtained in our laboratories have demonstrated that the limit values of the conversions depend both on the amount of catalyst and the temperature. This fact has led us to the conclusion that between the two process variables, the catalyst concentration and temperature, there is a certain interdependence.

Further it was analysed the influence of the molar ratio between the acrylic acid and epichlorohydrin on the yield both in the presence and without catalyst in the same reaction conditions (Fig. 3). As can be observed from the Fig. 3 the behaviour of the two systems is very different. Thus, in the presence of the catalyst (dotted lines) it may be noticed a yield rise with the increasing of the reactant ratio; this rising is more important in the case of acrylic acid excess. In these situation the increasing of yield would be taken into account on the increase of the amount of dissociated acid present in the system (acrylic acid is a weak acid partially dissociated).

The behaviour of the system is much more interesting in the presence of catalyst. Thus, one can observe a fast increase of the yield as the excess of epichlorohidrin rise that at a molar ratio epichlorohidrin : acrylic acid of 5 : 1 and 75°C the conversation reaches the maximum yield (100%) in about 1.5 h. But the behaviour of the catalytic system is different in the presence of an acrylic acid excess. Despite the expectations, with the increase of the molar ratio in the favour of acrylic acid it can be observed a significant decrease of the yield. The explanation consists both in the decrease of the epichlorohydrin concentration and especially due to the concentration of the dissociated species on the polymer surface, thus the probability of contacting the dissociated species with the epichlorohydrin is much more diminished.

Another objectiv of our study was to establish the influence of the structure of the quaternary ammonium compound. In this sense experiments where the monomer, dimethyldiallylammonium chloride, was used as catalyst, were performed. In Fig. 4 are represented the experimental data using the monomer as catalyst (5% concentration) comparatively with its polymer (dottes lines) taken in the same concentration. If one compares the results obtained with the two catalysts at 55°C, respectively 75°C, we can observe that dimethyldiallylammonium chloride shows a catalytic activity greater than the polymer. The same conclusions are obtained if we compare Fig. 4 to Fig. 2. Evidently, the major cause of the catalytic activity differences consists in the structural differences between the two catalyst and certainly we must not neglect neither the differences of kinetic mobility of the two catalytic species.

Another argument concerning the differences of kinetic mobility is based on the experimental data obtained with various polymer fractions for two reaction temperatures, 55°C and respectively 75°C. As it may be observed from the Fig. 5, the experimental data obtained for the two polymer fractions at 55°C fit on the same line while at 75°C there are some

differences in the behaviour of catalyst in the sense of the conversion increasing with the decrease of the molecular weight. Certainly their differences are due, probably, to both the mobility differences of macromolecules in the system and the mobility differences from the microbrownian

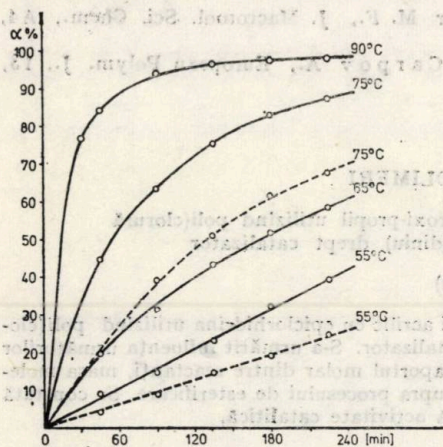


Fig. 4. — Influence of the catalyst concentration on the acrylic acid conversion at different reaction temperatures; molar ratio 1:1; catalyst concentration 5%; — monomer, --- polymer.

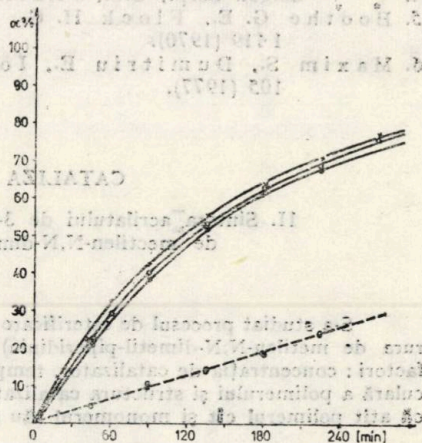


Fig. 5. — Conversion of acid against the molecular weight of polymer; x — $\bar{M}_v = 112\,000$; o — $\bar{M}_v = 416\,000$; ● — $\bar{M}_v = 724\,000$; molar ratio 1:1, reaction temperature: — 75°C, --- 55°C.

movement of the chain segments. Evidently these assertions assume a certain reserve due to the probability of some analytical errors but, in general, one can notice a different behaviour of the polymer fractions.

4. Conclusions

As general observations about the behaviour of the polymers having quaternary ammonium functions and used as catalyst in the esterification reaction of acrylic acid with epichlorohydrin it may be established the existence of a good catalytic activity which is influenced in some measure by the polymer structure.

A very important observation concern the possibility that a reactant species can concentrate on the polymer surface (acrylic acid in our case), fact which can explain the manner by which the catalyst is to act in this esterification process. Taking into account the two major possibilities of the polymers to act in the catalytic process either by catalytic functions (which are usually in the side chain) acting in the same manner as the micromolecular analogous or by the modification of the reaction medium structure due to the concentration of the one or both reactants on the polymer surface, we can suppose that poly(methylene-N,N-dimethylpiperidinium chloride) may be associated with the second mechanism.

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CATALIZA PRIN POLIMERI

II. Sinteza acrilatului de 3-clor-2-hidroxi-propil utilizând poli(clorură de metilen-N,N-dimetil-piperidiniu) drept catalizator

(Rezumat)

S-a studiat procesul de esterificare a acidului acrilic cu epiclorhidrina utilizând poli(clorură de metilen-N,N-dimetil-piperidiniu) drept catalizator. S-a urmărit influența următorilor factori: concentrația de catalizator, temperatura, raportul molar dintre reactanți, masa moleculară a polimerului și structura catalizatorului, asupra procesului de esterificare. Se constată că atât polimerul cât și monomerul său au o bună activitate catalitică.

SYNTHESIS AND UTILISATION OF *v*-METHYL-STYRENE-*p*-SULPHONATE (I)

BY

M. NICU

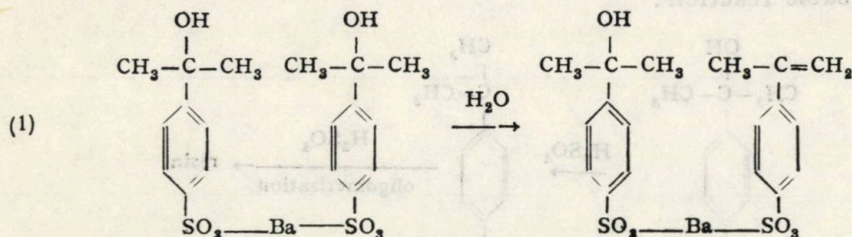
1. Introduction

Some directions of using the macromolecular compounds as adhesives, ion exchangers, elastomers, threads and fibres [1], [2] require polymers with strongly polar or even ionic groups which confer to the products adhesivity, solubility, hydrophilicity, chemical reactivity and higher tinctorial and antistatic properties.

Products with such properties may be obtained mainly by copolymerization. The comonomers with sulphonic groups, such as vinyl-sulphonate, allyl- and methallyl-sulphonate and *p*-styrene-sulphonate are particularly important. The vinyl-sulphonic monomers show some disadvantages for copolymerization and copolymers separation while styrene-sulphonate is unstable and shows unsatisfactory copolymerization constants. The synthesis and study of new sulphonic monomers is thus justified.

The studies were directed to the synthesis and characterization of *p*-isopropenyl-benzene-sulphonic acid and its salts (α -methyl-styrene-*p*-sulphonate) (MSS) because α -methyl-styrene (MS) and its starting compound isopropyl-benzene (IPB) are rather cheap.

Only one paper gives data on the MSS synthesis [3], where it is mentioned that barium *p*-isopropenyl-benzene-sulphonate was prepared by heating barium *p*-(α -oxyisopropyl)-benzene-sulphonate at 140°C, according to the reaction (1):



The trial of reproducing this synthesis has failed, only the crystallization water being removed.

In the method of obtaining MSS by treating the potassium *p*-(α -oxyisopropyl)-benzene-sulphonate with hydrogen chloride followed by dryness evaporation [3], the desired product could not be separated.

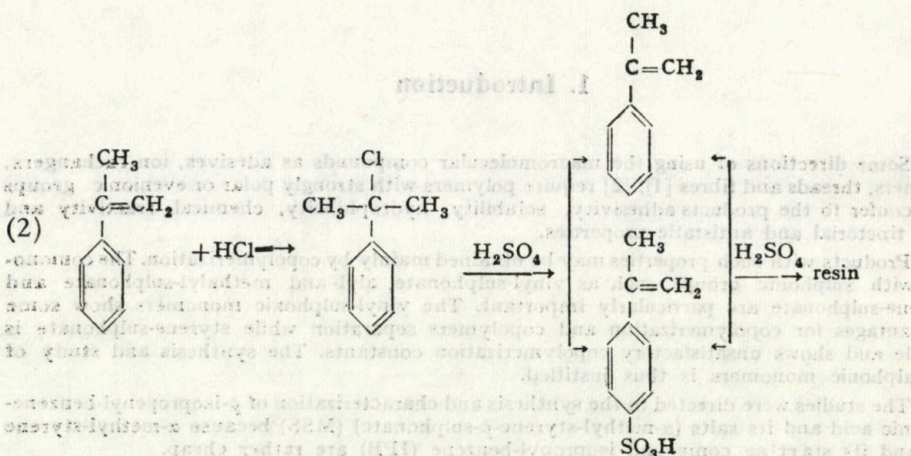
Consequently, it may be said that the above mentioned methods are not reliable, this conclusion being also drawn by Tiffeneau [4].

2. Possibilities of Synthetizing MSS

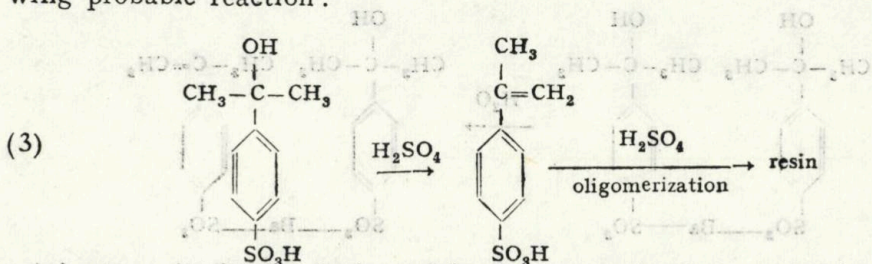
There are two ways of carrying out this synthesis, namely either the introduction of the precursor group for the double bond in the molecule, followed by the introduction of the sulphonic group, or conversely; in the third stage the double bond is formed (or reformed).

The following variants were investigated:

1. The double bond in MS was blocked by HCl addition, the product being then sulphonated. The sulphonation is accompanied by a dehydrochlorinating process, resulting in the formation of an unsaturated product which polymerizes in the reaction medium (H_2SO_4) with the formation of a black resin adhering to the vessel walls. Consequently, it is possible to consider that this synthesis was given up. The following reactions were supposed to proceed:



2. The dehydration of *p*-(α -hydroxy-isopropyl)-benzene-sulphonic acid was tried in sulphuric acid medium, but a resin was formed by the following probable reaction:

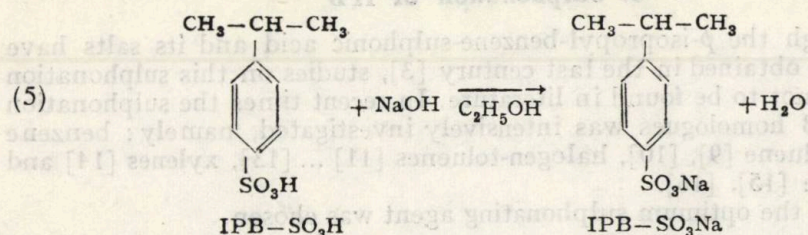
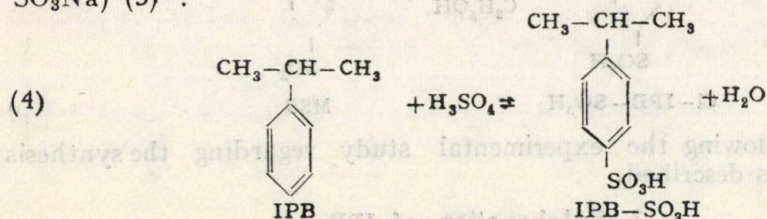


The following conclusions were drawn from the above experiments:

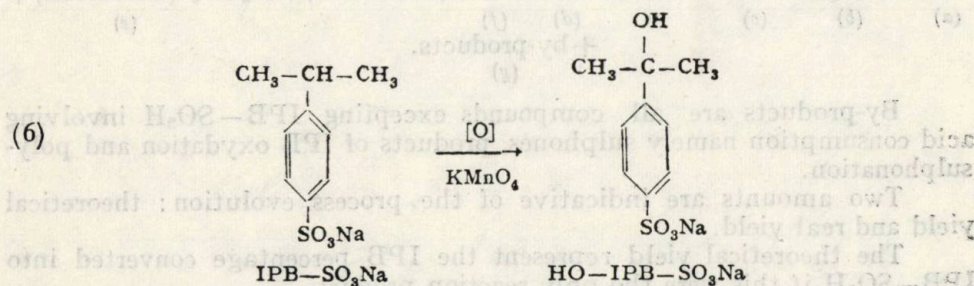
1. The MSS cannot be synthetized in acid medium due to the high cationic polymerization ability of MS and its derivatives.
2. The precursor group must lead to double bond only by a reaction in alkali medium; only halogens fulfil this condition.

3. The sulphonic group must be introduced in the ring before the formation of the precursor group of double bond.

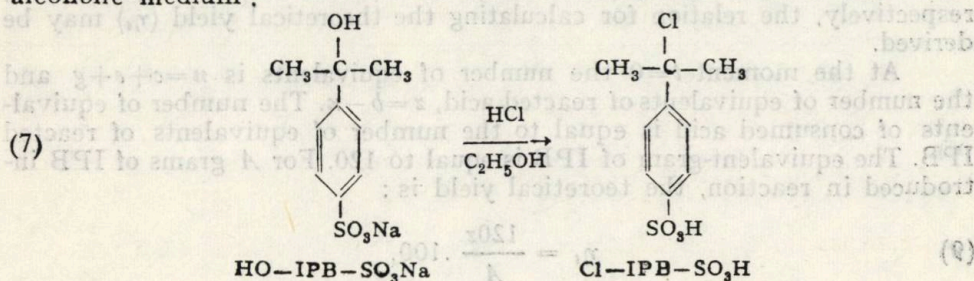
By taking these facts into account the synthesis was started with IPB which was sulphonated and the resulting *p*-isopropyl-benzene-sulphonic acid (IPB-SO₃H) (4) separated and purified as its alkaline salts (IPB-SO₃Na) (5):

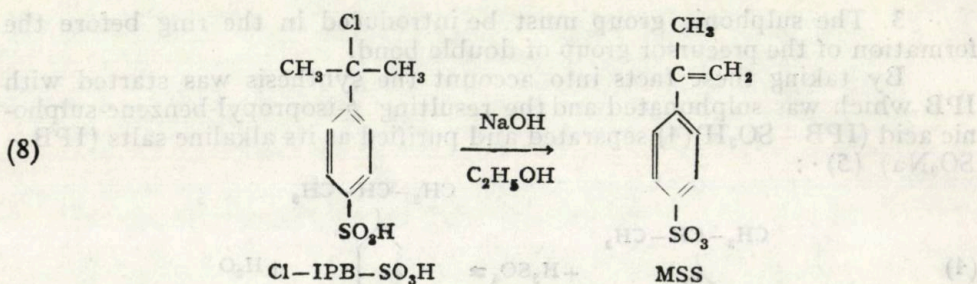


Since the IPB-SO₃Na (K) salts are soluble only in water and alcohol the halogenation could not be made directly. Consequently the halogen was introduced by substituting the hydroxy group in the α position which was previously formed by the oxydation of IPB-SO₃K by KMnO₄:



Finally, Cl-IPB-SO₃K was submitted to dehydrochlorination in alcoholic medium:





In the following the experimental study regarding the synthesis stage of MSS is described.

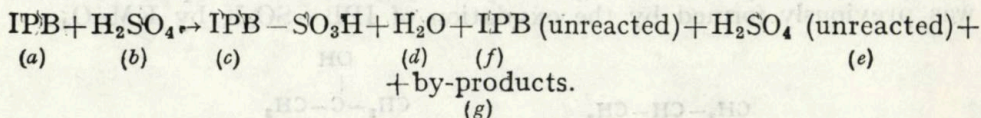
3. Sulphonation of IPB

Although the *p*-isopropyl-benzene-sulphonic acid and its salts have been already obtained in the last century [3], studies on this sulphonation reaction are not to be found in literature. In recent times the sulphonation of lower IPB homologues was intensively investigated, namely: benzene [5] ... [8], toluene [9], [10], halogen-toluenes [11] ... [13], xylenes [14] and ethyl-benzene [15], [16].

Firstly, the optimum sulphonating agent was chosen.

3.1. Experimental

The following reaction scheme may describe the sulphonation process:



By-products are all compounds excepting IPB-SO₃H involving acid consumption namely sulphones, products of IPB oxydation and polysulphonation.

Two amounts are indicative of the process evolution: theoretical yield and real yield.

The theoretical yield represent the IPB percentage converted into IPB-SO₃H if this were the only reaction product.

If *a*, *b*, *c*, *d*, *e*, *f* and *g* were the number of equivalents of IPB, H₂SO₄, IPB-SO₃H, H₂O, H₂SO₄ (unreacted), IPB (unreacted) and by-products, respectively, the relation for calculating the theoretical yield (η_t) may be derived.

At the moment $t=0$ the number of equivalents is $n=c+e+g$ and the number of equivalents of reacted acid, $z=b-n$. The number of equivalents of consumed acid is equal to the number of equivalents of reacted IPB. The equivalent-gram of IPB is equal to 120. For *A* grams of IPB introduced in reaction, the theoretical yield is:

$$(9) \quad \eta_t = \frac{120z}{A} \cdot 100,$$

where n is determined by titration.

The real yield (η_r) is proportional to the IPB amount converted into p -IPB- SO_3H which may be determined gravimetrically as p -IPB- SO_3K . The real yield is given by the relation:

$$(10) \quad \eta_r = \frac{120p}{256A} \cdot 100,$$

where 256 represent the molecular weight of IPB- $\text{SO}_3\text{K} \cdot \text{H}_2\text{O}$.

By comparing the theoretical and real yields the significance of side reactions may be estimated as well as the efficiency of consumption raw materials.

The IPB sulphonation may be carried out in either closed or open system according to water component (for the other components the system is always closed).

The content of *orto* and *para* isomers of the reaction product was estimated by NMR spectral measurements.

a) Determination of the Theoretical Yield in Closed Reaction System

In a three-neck flask of 100 ml provided with stirring and reflux condenser, introduced in a thermostated oil bath, the sulphonating agent was introduced in calculated amounts for a reaction volume of 30 ml. The IPB previously heated in the same oil bath was then added under stirring at a time taken as $t=0$ for the reaction.

When the reaction time was over, the reaction mixture was poured on 150 g ice in a glass of 500 ml. The flask was washed twice with 25 ml of distilled water.

The acid solution in the glass was titrated with aqueous KOH in the presence of phenolphthalein.

b) Determination of the Real Yield of Sulphonation in Closed Reaction System

In a three-neck flask of 250 ml, 30 g of IPB were sulphonated with sulphonating agent taken in calculated amounts. The reaction flask was then immersed in an ice bath. The cold reaction mixture was neutralized by a 2 M KOH methanolic solution in the presence of phenolphthalein. The suspension of the white precipitate thus formed was refluxed on a water bath and then filtered. The precipitate was taken in 100 ml methanol to recover IPB- SO_3K . The IPB- SO_3K crystallized in the methanolic solution was then purified by two recrystallizations from ethanol. After drying the salt crystallized with one water molecule was weighted (p).

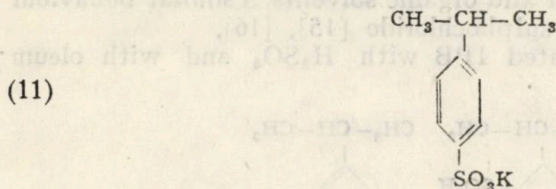
c) Determination of the Real Yield in Open Reaction System

The experiments were carried out as above, excepting the fact of using a Liebig cooler.

3.2. Chemical and Spectral Analyses

The elemental analyses of IPB- SO_3K (carbon and hydrogen contents) indicated the salt to be crystallized with one water molecule.

The IR and NMR spectra (Figs. 1 and 2) confirm the structure:



The spectra indicate the purified product to contain the *para* isomer only.

By NMR spectral measurements the *orto/para* ratio in the unpurified IPB-SO₃K was determined. In Fig. 2 the signals of methylic groups of the

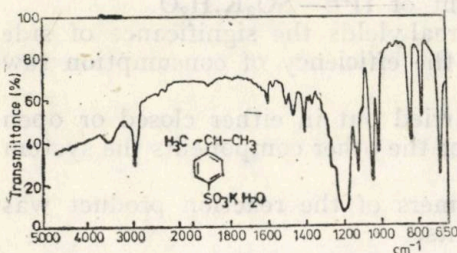


Fig. 1. — IR spectrum of *p*-IPB-SO₃K

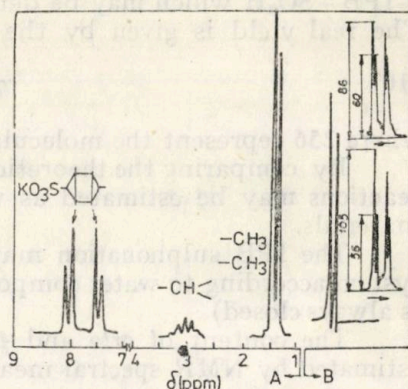


Fig. 2. — NMR spectrum of IPB-SO₃K: A — pure *p*-IPB-SO₃K, B — range of CH₃ signals of *orto-para* isomer mixture.

isomer mixture are given; the signals of protons in CH₃ group of *para* isomer give resonance at 1.0 and 1.17 ppm while those of the *orto* isomer at 1.04 and 1.15 ppm.

The sum of signal heights is: a) *para*, 86+105=191 mm; b) *orto*, 60+56=116 mm.

The molar percentage are:

$$\% \text{ mol } para = \frac{191}{191+116} = 62; \quad \% \text{ mol } orto = \frac{116}{191+116} = 38.$$

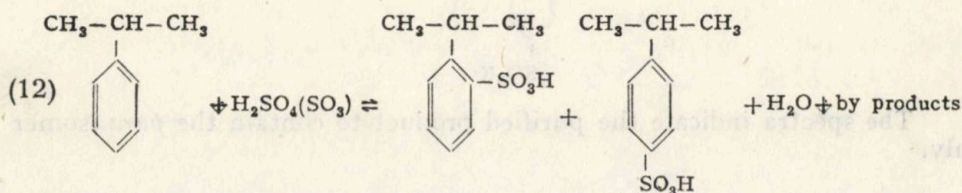
Similarly, the signals of other protons were also used.

3.3. Determination of the Optimum Sulphonating Reagent

The sulphonations with sulphuric acid, oleum and by means of chloro-sulphonic acid were studied.

The synthesis of IPB-SO₃H by chlorosulphonation was given up because during purification by distillation under vacuum (10 mm Hg) the sulphochloride decomposes violently releasing HCl and SO₂ with formation of a black resin insoluble in water and organic solvents. A similar behaviour was noticed with ethyl-benzene-sulphochloride [15], [16].

Consequently, we sulphonated IPB with H₂SO₄ and with oleum of different SO₃ contents:



The variation of the theoretical and real yield with the nature of sulphonating agent and the mole ratio of reactants was followed. The obtained data are listed in Table 1.

Table 1
Variation of the Yields with the Sulphonating Agent Nature

Sample	Sulphonating agent	SO ₃ introduced in the reaction moles	Mole ratio	Theoretical yield, [%]	Real yield %
21	H ₂ SO ₄ , $d = 1.831$	0.116	0.74	30.3	14.1
22	oleum 5% SO ₃	0.201	1.30	37.7	20.7
23	oleum 10% SO ₃	0.269	1.73	67.7	26.3
24	oleum 15% SO ₃	0.342	2.20	76.7	31.1
25	oleum 20% SO ₃	0.410	2.64	87.09	35.2

The theoretical yield increases with SO₃ concentration in the employed acid and with SO₃/IPB mole ratio. The real yield varies similarly but in a lesser extent.

The efficiency of acid consumption, calculated with the relation:

$$\text{Efficiency} = \frac{\text{real yield}}{\text{theoretical yield}},$$

gives an indication on the significance of side reactions and the direction of reactant consumptions.

The data plotted in Fig. 3 show the oleum 5% to be the optimum sulphonating agent, the side reactions being promoted by a higher SO₃ content. Besides, the cumen hydroperoxide formed by the oxidating action of oleum cause explosions.

It is more convenient to use concentrated H₂SO₄ instead of oleum of low SO₃ content; few by-products and in smaller amounts are thus formed.

4. Conclusions

1. It is not possible to synthesize MSS according to the literature indications.

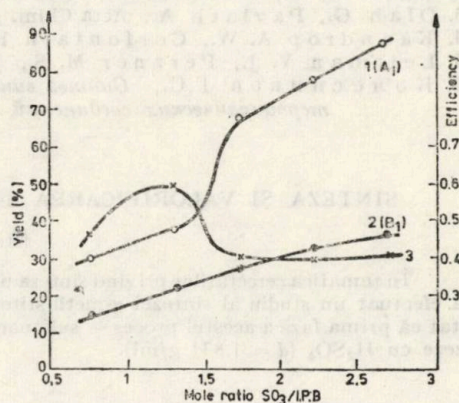


Fig. 3. — Influence of the nature of sulphonating agent on the theoretical yield (1), real yield (2) and efficiency of the acid consumption (3) in a closed reaction system, at 160°C and reaction time of 10 min.

2. Due to the great cationic polymerization capacity of α -methylstyrene and its derivatives the synthesis of MSS cannot be carried out in acid medium.

3. The precursor group of double bond must be a halogen.

4. The sulphonic group must be introduced into the ring before the precursor group of double bond.

5. The MSS synthesis was carried out by the following stages: IPB sulphonation, α -oxydation of the sulphonation product, substitution of hydroxy group by chlorine and dehydrochlorination.

6. Sulphuric acid ($d=1.831$ g/ml) is the most convenient sulphonat-agent.

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SINTEZA ȘI VALORIFICAREA α -METIL-STIRENULUI-*p*-SULFONAT (I)

(Rezumat)

În tematica cercetărilor privind sinteza unor monomeri cu grupe puternic polare sau ionici, s-a efectuat un studiu al sintezei α -metil-stirenului-*p*-sulfonat din izopropil-benzen. S-a constatat că prima fază a acestui proces — sulfonarea izopropil-benzenuului — este indicat să se realizeze cu H_2SO_4 ($d = 1,831$ g/ml).

MECHANOCHEMISCHE REAKTIONEN DES POLYVYNILCHLORIDS

6. DIE MODIFIZIERUNG DER POLYVYNILCHLORIDSUSPENSION (PVC-S) DURCH MECHANISCHEN ABBAU IM HOMOGENEN SYSTEM

VON

CLEOPATRA VASILIU-OPREA, FELICIA WEINER und ELENA TULEI

1. Einführung

In einer Reihe vorhergehender Arbeiten verfolgte man die Korrelation der morphologischen Kennzeichen des Polyvinylchlorids in Suspension (PVC-S) mit seinen Eigenschaften, sowie deren Verbesserung durch Ultraschallbehandlung im heterogenen System. Diese Behandlung hat als Resultat die Verkleinerung der geometrischen Abmessungen der Körner des erhaltenen Pulvers durch die Polymerisierung in Suspension und gleichzeitig die vorteilhafte Veränderung einiger Kennzeichen sowie: spezifische Oberfläche, Dichte, Weichmachersorption, Schwellgrad, Reißfestigkeit [1]...[5].

Zum Zweck der Kenntnis der erhaltenen Veränderungen der makromolekularen Kette des PVC-S unter dem Einfluß der akustischen Energie, studierte man die Ultraschallbehandlung von verdünnten und konzentrierten Lösungen des Polymers.

2. Experimentelle Untersuchungen

2.1. Studiumsobjekt und Ultraschallbehandlungstechnik

Polyvinylchloridsuspension mit den morphologischen und molekularen Eigenschaften aus [1] wurde für die Ultraschallbehandlung in Lösungen von Zyklohexanol von verschiedenen Konzentrationen verwendet. Das Lösungsmittel wurde kontinuierlich mit einer Destillationskollone gereinigt.

Der Ultraschallgenerator, Typ ULA-250, Tschechoslowakischer Fabrikation, stellt 1 MHz-Schwingungen bei einer Leistung von 341 W her. Als Kopplungsmedium der Energie der Ultraschallschwingungen verwendete man Transformatoröl. Die Glaszellen, in welcher die Polymerlösungen den Ultraschallschwingungen unterworfen waren, hatten parabolische Form und waren mit einem Verschlusssystem, Vakuumanlage und Thermostat versehen und in den US-Generator eingeführt. Bei allen US-Versuchen blieb das Lösungsmittelvolumen konstant und zwar 100 ml; als Arbeitsatmosphäre wurde Luft, ausschließlich der Fälle wo der Medieneinfluß studiert wurde, verwendet.

Als Hauptkriterium für die Beurteilung des mechanischen Abbaus zog man die Veränderung des Molekulargewichtes heran, welches durch zähltechnische Messungen laut [1], [2] bestimmt wurde.

2.2. Studium des Einflusses einiger Faktoren auf den mechanischen Abbauprozess durch Ultraschallbehandlung von PVC-S in Lösungen

Existieren mehrere Faktoren, die den Ultraschallbehandlungsprozeß in Lösungen beeinflussen, wobei Effizienz des Abbaus von der gleichzeitigen Aktion abhängt.

a) Einfluss der Ultraschallbehandlungsdauer

Um den Einfluß der Ultraschallbehandlungsdauer bezüglich der Veränderung des Molekulargewichtes zu verfolgen, verwendete man eine 1%-ige Lösung PVC-S in Zyklohexanon.

In Abb. 1 repräsentiert man die Veränderung des Molekulargewichtes

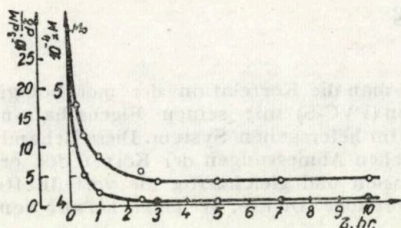


Abb. 1. — Änderung des Molekulargewichtes und der Abbaugeschwindigkeit in Abhängigkeit der Ultraschallbehandlungsdauer: 1 — Variation des Molekulargewichtes, 2 — Variation der Abbaugeschwindigkeit.

des Polymers in Abhängigkeit der Ultraschallbehandlungsdauer, sowie die Veränderung der Geschwindigkeit des mechanischen Abbauprozesses in der Zeit an. Man erkennt eine exponentielle Verkleinerung dieser Größe in Abhängigkeit der Ultraschallbehandlungsdauer laut der Baramboischen Gleichung [6].

$$(1) \quad M_{\tau} = (M_0 - M_{\infty})e^{-k\tau} + M_{\infty}.$$

Die Abbaugrenze für die obengenannten mechanischen Bedingungen für eine Temperatur von 20°C beträgt etwa 42 000, wobei der Anfangswert 57 000 betrug. Man kann dementsprechend

eine Verkleinerung der Abbaugeschwindigkeit in der Zeit feststellen, welche in den ersten Momenten des Abbaus am größten ist.

b) Einfluss der Temperatur

Der Verlauf des mechanischen Abbaus wurde auch für verschiedene Temperaturen studiert, wobei die erhaltenen Daten in den Abb. 2 und 3 angegeben sind. Der Verlauf dieser Kurven zeigt ebenfalls eine zeitliche Verkleinerung des Molekulargewichtes, bzw. der Viskositätszahl nach einem exponentiellen Gesetz.

Da sie kinetischen Werte vor dem Abbaugrenzwert für eine Temperatur von 20°C bekannt waren, konnte man der Abbaugrad (φ) und die Anzahl der gelösten Bindungen (Z) mit Hilfe folgender Gleichungen berechnen:

$$(2) \quad \varphi = \frac{\overline{M}_0 - \overline{M}_{\tau}}{\overline{M}_0 - \overline{M}_{\infty}} \cdot \frac{\overline{M}_{\infty}}{\overline{M}_{\tau}},$$

wobei: $\overline{M}_0$ — Anfangsmolekulargewicht des Polymers, $\overline{M}_t$ — Augenblicksmolekulargewicht, $\overline{M}_\infty$ — Abbaugrenzwert, φ — Abbaugrad;

$$(3) \quad Z = Z_m N,$$

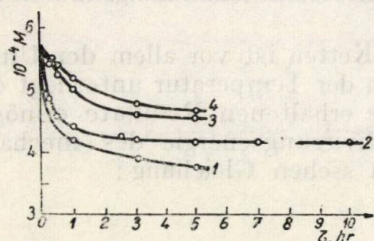


Abb. 2. — Änderung des Molekulargewichtes in Abhängigkeit der Ultraschallbehandlungsdauer für verschiedene Temperaturen: 1 — 5°C, 2 — 20°C, 3 — 60°C, 4 — 90°C.

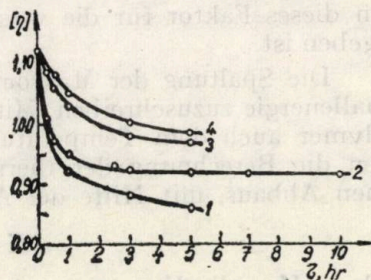


Abb. 3. — Änderung der Viskositätszahl $[\eta]$ in Abhängigkeit der Ultraschallbehandlungsdauer für verschiedene Temperaturen: 1 — 5°C, 2 — 20°C, 3 — 60°C, 4 — 90°C.

mit: Z — Gesamtzahl des zerstörten Bindungen, Z_m — Anzahl des zerstörten Bindungen eines Makromoleküls, N — Anzahl der Makromoleküle;

$$(4) \quad Z_m = \frac{[\eta_0]}{[\eta_t]} - 1,$$

worin: $[\eta_0]$ — Viskositätszahl der Ausgangslösung des Polymers, $[\eta_t]$ — Viskositätszahl der Lösung des mechanisch abgebauten Polymers im Augenblick t ;

$$(5) \quad N = N_1 \frac{m}{M},$$

wobei: N_1 — Loschmidt'sche Zahl, m — Masse, $[g]$, des zum Abbau unterworfenen Polymers, M — Molekulargewicht des Polymers.

Aus Abb. 4 kann man ein Anwachsen des Abbaugrades (φ) in der Zeit, sowie auch der Anzahl der gespaltenen Bindungen beobachten, was der Kurvenverlauf klar ausdrückt.

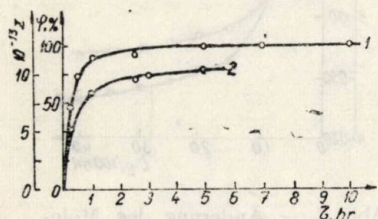


Abb. 4. — Änderung des Abbaugrades φ und der Anzahl der gespaltenen Bindungen in Abhängigkeit der Ultraschallbehandlungsdauer: 1 — Abbaugrad, 2 — Anzahl der gespaltenen Bindungen.

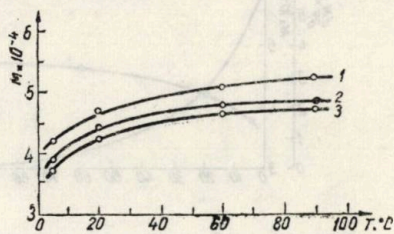


Abb. 5. — Änderung des Molekulargewichtes in Abhängigkeit der Ultraschallbehandlungstemperatur für verschiedene Behandlungsdauern: 1 — 0 Std., 2 — 3 Std., 3 — 5 Std.

Man kann feststellen daß die Temperatur einen wesentlichen Einfluß im Ultraschallbehandlungsprozeß hat. Deren Veränderung ist ausschlaggebend für die Effizienz des mechanischen Abbaus, was klar aus Abb. 5 hervorgeht, in welcher die Änderung des Molekulargewichtes als Funktion dieses Faktor für die verschiedene Ultraschallbehandlungsdauern angegeben ist.

Die Spaltung der Makromolekularen Ketten ist vor allem der Ultraschallenergie zuzuschreiben. Mit Anwachsen der Temperatur unterliegt das Polymer auch dem Temperaturabbau. Die erhaltenen Resultate ermöglichen die Berechnung der thermischen Aktivierungsenergie des mechanischen Abbaus, mit Hilfe der Arrhenius'schen Gleichung:

$$(6) \quad K = K_0 e^{-E_a/RT},$$

wobei: K — die Konstante der mechanischen Abbaureaktionsgeschwindigkeit, K_0 — vorexponentieller, temperaturabhängiger Faktor, R — universelle Konstante der Gase, E_a — Aktivierungsenergie.

Die Konstante K wurde aus der Baramboim'schen Gleichung abgeleitet und zwar:

$$\bar{M}_\tau = (\bar{M}_0 - M_\infty) e^{-K\tau} + \bar{M}_\infty,$$

woraus:

$$K = \frac{1}{\tau} \ln \frac{\bar{M}_\tau - M_\infty}{\bar{M}_0 - M_\infty}.$$

Es wurde die Aktivierungsenergie für $\tau = 1$ Std. = 3 600 s berechnet. Aus der graphischen Darstellung der Gleichung:

$$\ln K = \ln K_0 - E_a/RT,$$

leitet man den Wert von E_a ab, unter Bezugnahme der Parameter der erhaltenen Geraden. Es folgt: $E_a = 1,805$ Kcal/mol und $K_0 = 0,0187$.

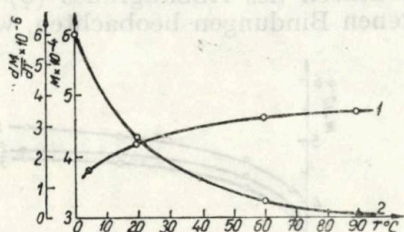


Abb. 6. — Änderung der Geschwindigkeit von Molekulargewichtsverringierung: 1 — Änderung des Molekulargewichtes in Abhängigkeit von Temperatur, 2 — Änderung der Geschwindigkeit von Molekulargewichtsverringierung in Abhängigkeit der Temperatur.

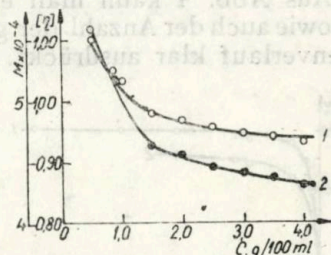


Abb. 7. — Änderung des Molekulargewichtes in Abhängigkeit der Konzentration: 1 — Molekulargewicht, 2 — Viskositätsveränderung.

Man kann feststellen daß der Wert der Aktivierungsenergie extrem klein, fast vernachlässigbar ist, was beweist daß die Hauptrolle des Abbaus der mechanischen Energie zufällt.

In Abb. 6 ist die Änderung des Molekulargewichtes in Abhängigkeit der Temperatur, für eine gleiche Ultraschallbehandlungsdauer ($\tau=5$ Std.) angegeben. Die temperaturabhängige Geschwindigkeitsverringern der Änderung diese Kennwertes ist augenfällig.

c) Einfluss der Konzentration

Um eine naturgetreue Darstellung bezüglich des mechanisch-chemischen Abbaumechanismus in Lösungen zu erhalten, muß man von dem Zustand der Moleküle in Lösungen ausgehen, der vor allem der von der Konzentration und der Güte des Lösungsmittels abhängt. Man verfolgte die Molekulargewichtsänderung für eine Konzentrationsintervall von 0,5 bis 4%, wobei man eine Abnahme mit der Konzentrationsvergrößerung feststellen konnte (Abb. 7).

Um eine möglichst komplette Charakterisierung des konzentrationsabhängigen mechanischen Abbauvorganges zu erhalten, bestimmte man die kinetischen Kurven für jeden Wert dieser Größe und vergleichsmässig mit der Anzahl der jedmally gesprengten Bindungen, welche in Abb. 8 wiedergegeben sind.

Verfolgt man diese Verläufe folgt eine interessante Tatsache, und zwar, daß unter dem Einfluß der Ultraschallwellen der mechanische Abbau intensiver in konzentrierten Lösungen ist (Kurven 1...10), wobei die Anzahl der gesprengten Bindungen maximal für $c=4\%$ ist (Kurve 10, vergleichsmässig mit Kurven 6...9).

Diese Resultate stimmen gut mit denen der Fachliteratur überein wo behauptet wird daß der mechanochemische Abbau der Polymerlösungen stärker für verwickelte Ketten als für gereckte ist [8] ... [10].

Bei kleinen Konzentrationen erscheinen die makromolekularen Ketten als lockere, geöffnete Knäuel, wobei die intra- und inter-Ketteninteraktionen schwach sind. Aus diesem Grund, als System genommen, weisen sie eine große Elastizität auf und die mechanische Energie konzentriert sich statistisch auf eine kleine Anzahl von chemischen Bindungen. Die mechanischen

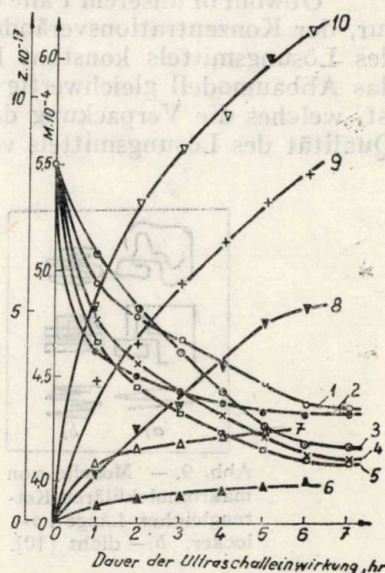


Abb. 8. — Änderung des Molekulargewichtes und der Anzahl der gespaltenen Bindungen im inerten Medium in Abhängigkeit der Ultraschallbehandlungsdauer für verschiedene Konzentrationen: 1...5 — Zeit-Variationskurven des Molekulargewichtes für verschiedene konstante Konzentrationen; 6...10 — desgleichen, der Anzahl der gespaltenen Bindungen.

Schwingungen, die durch die Fortpflanzung der Ultraschallwellen entstehen begegnen praktisch eine kleine Anzahl von Kettenabschnitten deren Achse mit der mechanischen Kraftwirkung übereinstimmt. Aus diesem Grund verliert sich der größte Teil der elastischen Energie, sowie die Schallwelle oder thermische Einwirkung in der umhüllenden Flüssigkeit und nur ein kleiner Teil konzentriert sich auf die Ketten und führt zu deren Abspaltung.

Dagegen, beim Anwachsen der Konzentration, der intra- und inter-Ketteninteraktionen wegen, die intensiver werden, erscheinen die kinetischen Einheiten (Knäuel oder kleinere und größere Zuschlagstoffe, die aus deren Verwirren entstehen) als Formationen mit größerer Verpackungsdichte, mit größerer Steifigkeit, was zu mehreren Konzentrationmöglichkeiten der mechanischen Energie führt. In diesem Fall wird die Anzahl der Kettenabschnitte in der Fortpflanzungsrichtung der mechanischen Kraft mehr und mehr anwachsen, was zu einem Anstieg, der Eigenabspaltung führt. Die Energieverluste im Medium verkleinern sich, was zu einem besseren Übergangsgrad der mechanischen in chemische Energie führt.

Obwohl in unserem Falle die Knäuel mit dichter oder lockerer Struktur, der Konzentrationsveränderung wegen erhalten werden, wobei die Art des Lösungsmittels konstant bleibt (Cyklohexanol), nehmen wir an daß das Abbaumodell gleichwertig mit dem von Minoura vorgeschlagenen ist, welches die Verpackung der kinetischen Energie verändert, wobei die Qualität des Lösungsmittels verändert wird (Abb. 9) [10].

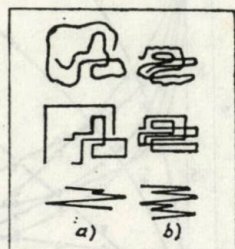


Abb. 9. — Modelle von makromolekulären Ketten gleicher Länge: a) — locker, b) — dicht [10].

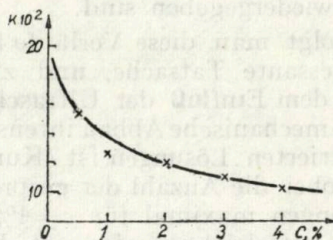


Abb. 10 — Abhängigkeit der Konstante der mechanischen Abbaugeschwindigkeit durch Ultraschallbehandlung von der Konzentration der Lösung.

Man könnte annehmen, daß bei essentiell verschiedenen Konzentrationen auch der Abbauplatz anderes ist. Im Falle der verdünnten Lösungen kann man annehmen, daß der mechanische Abbau hauptsächlich im abgeschiedenen Film an der Oberfläche der Kavitationsblase fortläuft. Eine wichtige Rolle kommt auch den pulsierenden Blasen in Resonanz zu, welche die Kette schwächen und verformen, sodaß sich diese im Augenblick des Platzens der Kavitationsblase abspaltet. Die makromolekularen Ketten, die diesem monomolekularen Film benachbart sind, welcher die Abscheidungs-grenze der Kavitationsblasen-Reaktionsmedium bildet, leiden sofort unter dem Einfluß der aktiven Teilchen, die sowie aus der Literatur [11]

bekannt ist, in der Kavitationsblase entstehen und sich in die Flüssigkeit bei deren Platzen fortpflanzen.

Für die konzentrierten Lösungen ist die Schockwelle, welches sich durch die Polymerlösung im Augenblick des Platzens der Kavitationsblase bildet und fortpflanzt von maximaler Effizienz.

Die Resultate aus Abb. 10, welche die Werte der Abbaugeschwindigkeits konstante mit der Konzentration korrelieren, zeigen, daß obwohl bei verdünnten Lösungen die Abbaugrenze kleiner ist, erhält man diese schneller, da in diesem Fall die Reaktionsgeschwindigkeit größer ist. Die konzentrierten Lösungen erleiden einen tiefwirkenderen Abbauprozess, die Abbaugrenze $\bar{M}_\infty$ ist größer, aber die Abbaugeschwindigkeit kleiner. Dieses Resultat muß wegen dem Anwachsen des Widerstandes des Mediums bei Konzentrationserhöhung erklärt werden, da der Eintritt der mechanischen Energie gleichbleibt.

d) Einfluss des Mediums

Um Informationen betreffs der Kinetik und vor allem bezüglich des Mechanismus des mechanischen Abbaus in Lösungen zu erhalten, wurden die Reaktionen sowohl in Edelgasatmosphäre (Argon) als auch in Beisein von aktiven Gasen, sowie Sauerstoff (aus der Luft) und DPPH in Form von alkoholischer Lösung, durchgeführt.

Die Kurven 1 ... 3 (Abb. 11) beschreiben die Verkleinerung des Molekulargewichtes nach einem exponentiellen Gesetz und zeigen, daß der mechanochemische Abbau sich mit größter Effizienz im Beisein von DPPH (Kurve 3) abspielt. Die Kurven 4 ... 6 definieren die Variation der abgespaltenen Bindungen und sind in guter Übereinstimmung mit denen, die Variation des Molekulargewichtes darstellen. In Edelgasatmosphäre ist der mechanische Abbau am kleinsten und der Sauerstoff nimmt eine Mittelstellung bezüglich seines Einflusses ein.

Auf Grund dieser Resultate kann man aussagen, daß im inerten Medium die freien Makromolekülreste sich durch verschiedene Reaktionen verbrauchen können, sowie Rekombination-Disproportionierung Übertragung, die in aktiven Medien durch die schnelle Bindung des Reaktionspartners an den Enden der aktiven Abbaufragmenten verhindert sind.

Mechanisch, durch Ultraschallwellen abgebautes Polyvinylchlorid in verschiedenen Medien wurde bezüglich des Temperaturverhaltens, durch die thermogravimetrische und thermodifferenzielle Analyse charakterisiert. Für diese Analyse wurden 3-stündig Ultraschallbehandelte Proben in verschiedenen Medien ausgewählt. Die erhaltenen Resultate sind in Abb. 12 wiedergegeben.

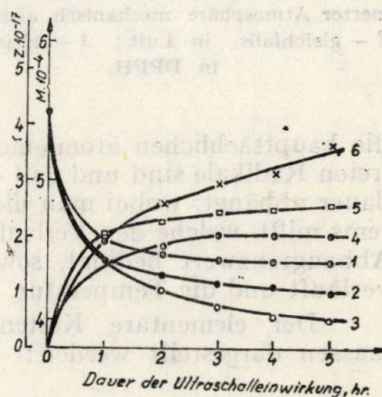


Abb. 11. — Änderung des Molekulargewichtes und der Anzahl der abgespaltenen Bindungen in Abhängigkeit der Ultraschallbehandlungsdauer im Beisein von verschiedenen Radikalakzeptoren: 1...3 — Änderung des Molekulargewichtes, 4...6 — Änderung der Anzahl der abgespaltenen Bindungen.

Man kann feststellen daß die mechanisch abgebauten Proben im inerten Medium, die durch einen kleinen Abbaugrad charakterisiert sind, vom thermischen Gesichtspunkt aus am stabilsten sind. Sie weisen den kleinsten Gewichtsverlust in Abhängigkeit der thermischen Abbautemperatur auf (Abb. 12, Kurve 1). Alle drei

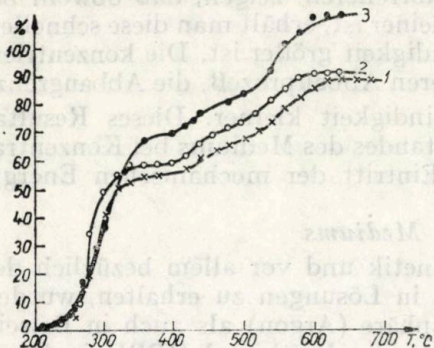


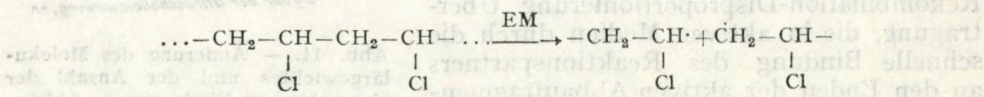
Abb. 12. — Änderung der Gewichtsverluste ultraschallbehandelter Proben in Lösungen für eine Behandlungsdauer von 5 Stunden mit der Abbautemperatur: 1 — PVC-S in inerter Atmosphäre mechanisch abgebaut, 2 — gleichfalls, in Luft; 3 — gleichfalls in DPPH.

Kurven beweisen, daß für die thermische Stabilität vor allem das erhaltene Molekulargewicht im Beisein von verschiedenen Medien und weniger deren chemische Natur bedeutend sind. Somit, obwohl die chemische Bindung des DPPH an die Abbaufragmente die Bildung einer neuen Verbindung bedeutet, die die Makromoleküle dieses Mediums beinhaltet, also eine zyklische Einheit, die thermostabilitätssichernd sein soll, hat trotzdem von diesem Gesichtspunkt aus das mechanisch abgebaute Polymer in Gegenwart vom Luftsauerstoff (Kurve 2 verhältnismässig der Kurve 3) ein besseres Verhalten.

3. Diskussion und Deutung der Ergebnisse

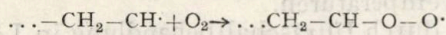
Aus den gesamten erhaltenen Resultaten kann man behaupten, daß die hauptsächlichsten atomo-molekulären Veränderungen das Abspalten der freien Radikale sind und daß deren Anzahl von der Ultraschallbehandlungsdauer abhängt, wobei man die mechanisch akkumulierte Energie des Systems mißt, welche den Verlauf mit einer gewissen Geschwindigkeit bis zum Abbaugrenzwert bedingt, sowie die Gasatmosphäre in der die Reaktion verläuft und die Temperatur.

Der elementäre Kettenradikalabbaumechanismus kann folgendermassen dargestellt werden:

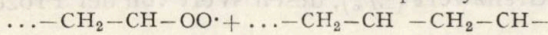


Die IR-Spektroskopie zeigt, daß der mechanische Abbau zu der Änderung der Kettenkonformation und zu der Verkleinerung des Chlorabsorptionsstreifens (695 cm^{-1}) und seiner Harmoniken von 1500 cm^{-1} führt [4]. Wenn die Ultraschallbehandlungsdauer lang ist und diese im Beisein von Radikalakzeptoren verläuft, reagieren die erhaltenen Makroradikale mit diesen und das Polyvinylchlorid erhält neue funktionelle dem Ausgangspolymers nichtspezifische Gruppen, in unserem Fall DPPH oder oxydierte Gruppen, wegen dem Einfluß des Luftsauerstoffs.

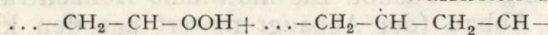
Die Daten der vorliegenden Arbeit und von [1] ... [5] beweisen daß sich folgender mechanochemischer Abbaumechanismus im Beisein des Luftsauerstoffs vollführt, und zwar:



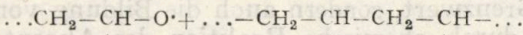
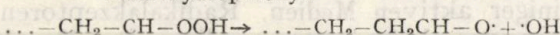
peroxydiertes Makroradikal



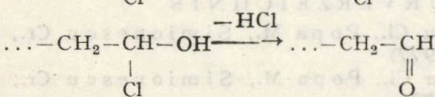
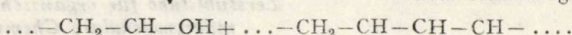
Wasserstoffübergang



Makrohydroperoxyd

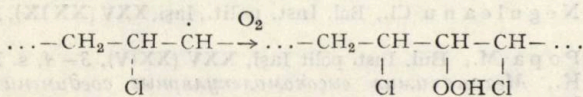


Wasserstoffübergang



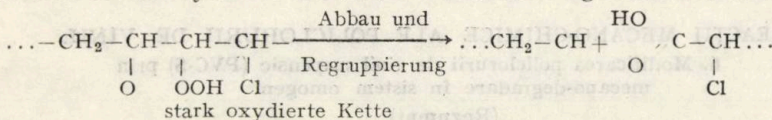
Makromolekül mit Carbonylgruppe

oder Makroradikale der Form:



durch Peroxydierung
und Hydroperoxydierung

In den Endstadien des mechanischen Abbaus im Beisein von Sauerstoff können stark oxydierte Ketten, die nachher folgendermassen abspalten:



erscheinen, was das Erscheinen einer neuen funktionellen Kettengruppe erklärt. Dieser Mechanismus, nach unserer Meinung, ist auch für die chemischen Veränderungen im Gebrauch verantwortlich, was zum Dauerbruch und Altern des Polymers führt.

4. Schlußfolgerungen

1. Der mechanochemische Abbau durch Ultraschallbehandlung in Lösungen von PVC-S ist von einer Reihe von Faktoren und zwar: Ultra-

challbehandlungsdauer, Temperatur, Konzentration der Lösung und der Natur des Mediums bedingt.

2. Der mechanische Abbau durch Ultraschallbehandlung in Lösungen ist maximal für die minimalen Temperaturen.

3. Der mechanische Abbau durch Ultraschallbehandlung in Lösungen hat als hauptsächlichste Ursache die Verringerung des Molekulargewichtes bis zu einem bestimmten Grenzwert ($\bar{M}_\infty$), dessen Wert von der Prozeßdauer abhängt.

4. Der mechanische Abbau hängt im bedeutendsten Maßstab von der Konzentration der Lösung ab, welche den bedeutendsten Einfluß auf die Reaktionsgeschwindigkeit ausübt. Die maximale Konzentration ermöglicht den maximalen Abbau (der Abbaugrenzwert hat den kleinsten Wert) und die kleinste Geschwindigkeit.

5. Der mechanische Abbau durch Ultraschallbehandlung von PVC-S Lösungen im Beisein einiger aktiven Medien, Radikalakzeptoren (Luftsauerstoff, DPPH) ist intensiver als im inerten medium. Das Resultat der Reaktion in dieser Fall ist nicht nur die Verringerung des Molekulargewichtes bis zu einem bestimmten Grenzwert, sondern auch die Bildung von neuen funktionellen Endgruppen durch chemische Reaktion des Akzeptors mit den aktiven Abbaufragmenten.

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Lehrstuhl für organische und
makromolekulare Chemie

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REAȚII MECANO-CHIMICE ALE POLICLORURII DE VINIL

6. Modificarea policlorurii de vinil suspensie (PVC-S) prin mecano-degradare în sistem omogen

(Rezumat)

Se descriu rezultatele cercetărilor privind mecano-degradarea policlorurii de vinil obținute prin polimerizarea în suspensie (PVC-S) având ca scop elucidarea reacțiilor ce decurg la nivel molecular prin solicitarea mecanică a acestui polimer. Datele obținute dovedesc dependența procesului mecano-distructiv de o serie de factori precum: durata, temperatura, natura mediului, concentrația soluției.

Un rezultat ce trebuie relevat este cel referitor la sensul influenței concentrației. Numeroase date din literatură susțin ideea că eficacitatea mecano-degradării în soluție este maximă pentru concentrații minime. În cazul PVC-S rezultatul obținut este invers și concordă cu rezultatele și reprezentarea dată procesului de către Y. Minoura și colaboratori [8].

RECENZII

BOOK REVIEWS

РЕЦЕНЗИИ

* * * *L'Informatore Farmaceutico* 1981. Vol. I, Vol. II, Organizzazione Editoriale Medico-Farmaceutica, Milano, 1981, 1700 pp.

Das italienische Medikamentenjahrbuch stellt alle Medikamentenspezialitäten und chemischen Substanzen vor, die im Jahr 1981 produziert wurden.

Der erste Band enthält in alphabetischer Reihenfolge alle Erzeugnisse, ihre Zusammensetzungen, die pharmazeutische Form und therapeutische Anweisungen. Zu jedem Produkt findet man Angaben betreffs der Rezepte und der Aufbewahrung. Weiter werden in alphabetischer Reihenfolge diagnostische, kosmetische, diätetische und medizinisch-technische Produkte vorgestellt. Die Ausgangsstoffe sind mit den Adressen der Lieferanten versehen.

In II. Band sind die pharmazeutischen Substanzen mit den lateinischen Bezeichnungen versehen, werden therapeutische Anweisungen gegeben und die Arzneimittel angegeben in denen sie zu finden sind.

Die großen Krankheitsgruppen sind kodifiziert und für jede sind die notwendigen Medikamente vorgesehen. Im diesem Band sind die Hersteller der Medikamente, der kosmetischen und diätetischen Produkte enthalten; weiter werden Systeme von Mikrofiches für die Medikamentenübersicht und die Spezialliteratur des Verlages OEMF vorgestellt.

Man kann sich leicht über alle Medikamente, über die diagnostischen, kosmetischen und diätetischen Erzeugnisse informieren, auch weil diese mit englischem Text versehen sind.

Das Medikamentenjahrbuch liefert wesentliche und praxisbezogene Daten über die Medikamente, so daß es besonders nützlich ist sowohl für Ärzte als auch für Apotheker.

El. Gafițanu

COLOMBO M. B., *Control of Physical Properties in Pharmaceutical Forms*. Organizzazione Editoriale Medico-Farmaceutica, Milano, 283 pp.

Das Buch liefert einen wichtigen Beitrag zur Kontrolle der spezifischen physikalischen Konstanten pharmazeutischer Formen.

Die Verbesserung der Technologie bei der Herstellung pharmazeutischer Erzeugnisse wird auch bestimmt durch die erreichten Fortschritte auf dem Gebiet der Kontrolle der verschiedenen, durch die pharmazeutische Form vorgeschriebenen Parameter. Neben der Bestimmung des Gehalts an aktiven Substanzen sind Bestimmungen notwendig betreffs der Definition der physikalischen Eigenschaften, die die Möglichkeit einer Beurteilung der Stabilität des Arzneimittels bietet.

Die Qualität der pharmazeutischen Form wird nicht nur durch die Quantität der aktiven Substanz beurteilt, sondern auch durch eine Reihe von Kennziffern, die die pharmazeutische Wirksamkeit bis zur Verabreichung des Medikaments sichern sollten.

Der Verfasser beschreibt detailliert die Methoden und notwendigen Apparate der physikalischen Kontrolle aller pharmazeutischer Formen. Die Auswahl der nötigen Tests einer pharmazeutischen Form berücksichtigt die Notwendigkeit, die therapeutische Aktivität des Arzneimittelpräparats zu garantieren.

Die Arbeit ist in 7 Teile untergliedert. Im ersten Teil sind alle pharmazeutischen Formen kodifiziert, während der 2. Teil die Definitionen dieser enthält. Die eigentliche Kontrolle jeder dieser pharmazeutischen Formen wird auf je einer Kontrollkarte beschrieben. Jede Kontrollkarte enthält außerdem den Kode der physikalischen Eigenschaften, dem eine Addendumnummer entspricht, sowie die Titel und Seiten, wo diese im Buch zu finden sind.

Der 4. Teil der Arbeit enthält eine Klassifikation aller pharmazeutischen Formen hinsichtlich der gemeinsamen Eigenschaften oder der spezifischen jeder dieser Formen.

Der folgende Teil besteht aus dem Addendum, in dem alle in den Kontrollkarten erwähnten physikalischen Methoden wiedergegeben sind.

Im 6. Teil der Arbeit werden eine Reihe von Tabellen angegeben, nützlich für die physikalischen Bestimmungen.

Die Arbeit schließt mit einem Wörterverzeichnis der in der Pharmazietechnik angewendeten technischen Fachausdrücke mit italienischer, französischer, spanischer und deutscher Übersetzung.

Der klare, kurzgefaßte Stil, in dem das Buch geschrieben ist, gestattet jedem Forscher die Auswahl von Kontrollmethoden entsprechend der pharmazeutischen Form mit allen möglichen Eigenschaften.

Die zusammengestellten technischen Aspekte in zugänglicher Form schließen Kenntnisse ein, die das Interesse für die Anwendung der Arbeit vergrößern.

El. Gafițanu

HARBORNE J. B., VAN SUMERE C. F., *The Chemistry and Biochemistry of Plant Proteins*, Gent.

În colecția Dări de seamă ale simpozionului Societății de fitochimie, Universitatea din Gent, Belgia, a apărut o lucrare valoroasă în care un număr de 19 specialiști din Anglia, Belgia Franța, R.D.G., R.F.G., S.U.A. prezintă o serie de studii efectuate în domeniul chimiei și biochimiei proteinelor de origine vegetală.

În primul capitol se prezintă analiza secvenței aminoacizilor din proteine insistându-se asupra purificării proteinelor, fracționării lor, separării peptidelor etc. Se arată, în general, că la solubilizarea și fracționarea proteinelor din cereale se întâmpină încă mari dificultăți tehnice.

Capitolul 2, redactat de J. Daussant, cuprinde imunochimia, o tehnică relativ nouă ce se poate aplica la separarea și studiul proteinelor din semințe.

În al treilea capitol, Hermann Stegemann tratează despre proprietățile și modificările fiziologice în proteinele de rezervă din cereale și tuberculii de cartof.

Următorul capitol se ocupă de proteinele din orz și factorii ce influențează acumularea lor.

Orio Ciferri prezintă în capitolul 5 mecanismul sintezei proteinelor la plantele superioare.

Biogeneza mitocondriilor din plante și a cloroplastelor precum și structura și funcționarea lor reprezintă conținutul capitolelor 6 și 7.

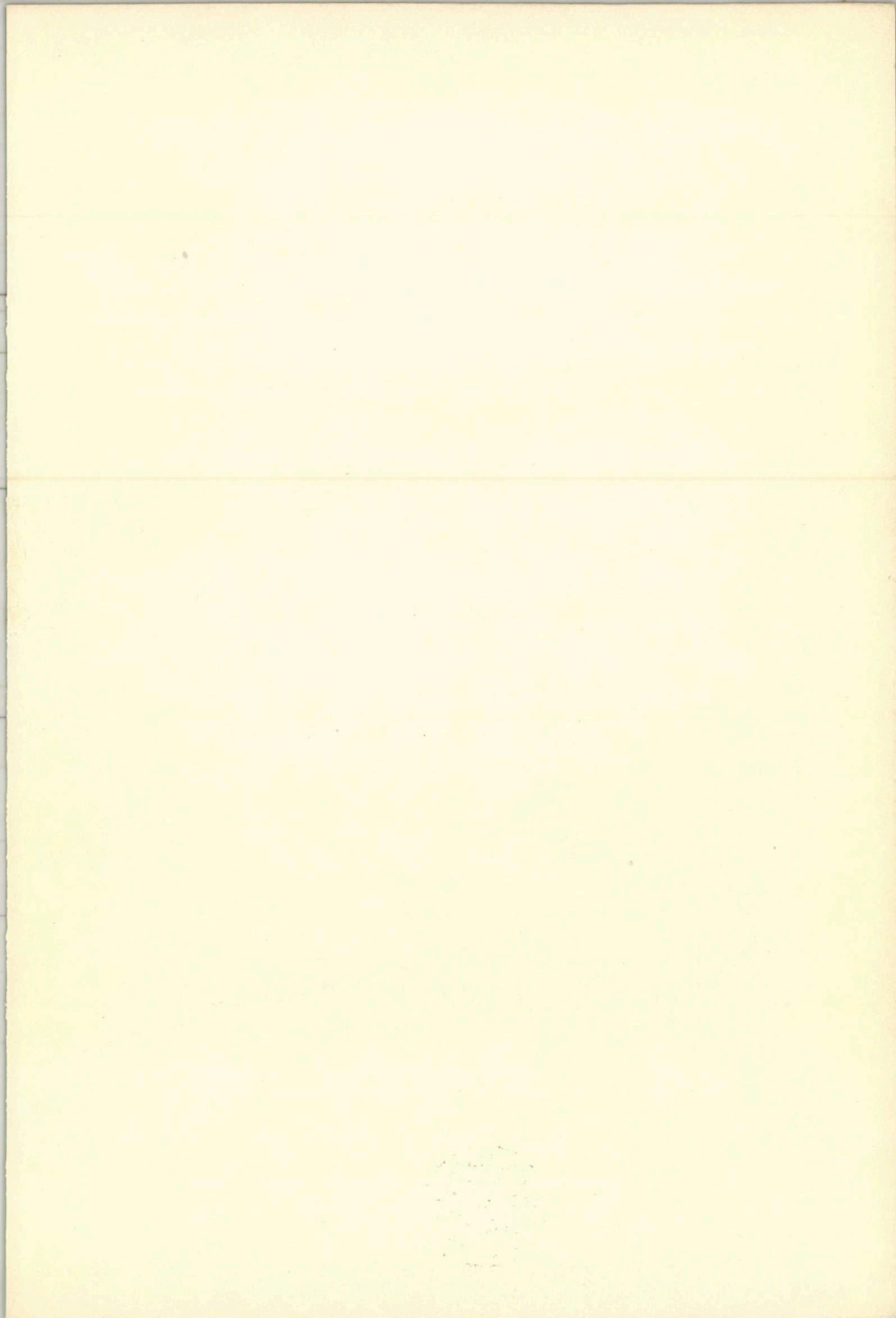
Capitolul 8 se referă la interacțiunea între fenolii și proteinele din plante, rezistența plantelor față de factorii fitopatogeni precum și rolul fenolilor și a proteinelor în formarea humusului

Ultimele două capitole se referă la studiul macromoleculor proteice și clasificarea proteinelor vegetale.

Având în vedere importanța deosebită a proteinelor vegetale considerăm că lucrarea trebuie consultată de specialiștii ce lucrează în domeniul biochimiei, fiziologiei, agrochimiei, chimiei organice etc.

Ionela Popescu





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